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(54) **IMAGE-FORMING METHOD USING HEAT-SENSITIVE TRANSFER SYSTEM**

(75) Inventors: **Kazuaki Oguma**, Minami-ashigara (JP); **Yoshio Ishii**, Minami-ashigara (JP); **Kazuma Takeno**, Minami-ashigara (JP); **Hisashi Mikoshiba**, Minami-ashigara (JP); **Yoshihisa Tsukada**, Minami-ashigara (JP)

(73) Assignee: **FUJIFILM Corporation**, Tokyo (JP)

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See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,071,823 A * 12/1991 Matsushita et al. 503/227
5,393,726 A * 2/1995 Graumann 503/227
6,372,689 B1 * 4/2002 Kuga et al. 503/227
7,223,513 B2 * 5/2007 Nakane et al. 430/200

FOREIGN PATENT DOCUMENTS

JP 6-270559 9/1994

* cited by examiner

Primary Examiner—Richard L. Schilling
(74) *Attorney, Agent, or Firm*—Sughrue Mion, PLLC

(57) **ABSTRACT**

An image-forming method, containing the steps of: superposing a heat-sensitive transfer sheet on a heat-sensitive transfer image-receiving sheet so that the following at least one receptor layer of the heat-sensitive transfer image-receiving sheet can be contacted with the following thermal transfer layer of the heat-sensitive transfer sheet; and providing thermal energy given by a thermal head in accordance with image signals, thereby to form an image; wherein the heat-sensitive transfer image-receiving sheet is transported at a speed of 125 mm/s or more during the image formation, and wherein the heat-sensitive transfer image-receiving sheet contains, on a support, at least one receptor layer containing a polymer latex, and at least one heat insulation layer containing hollow polymer particles but free of any resins having poor resistance to an organic solvent except for the hollow polymer particles, and the heat-sensitive transfer sheet contains, on a support, a thermal transfer layer.

4 Claims, 1 Drawing Sheet

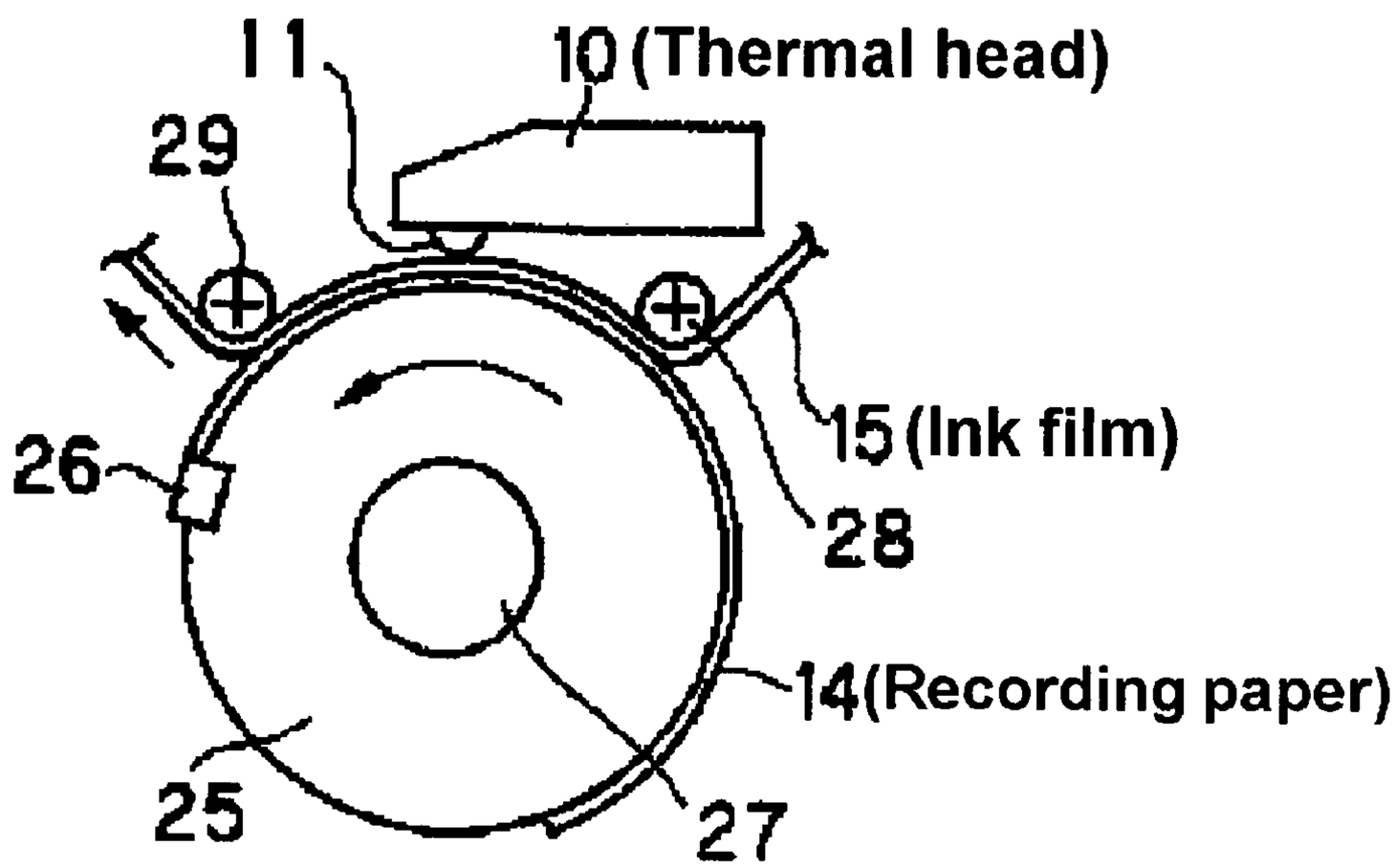


Fig. 1

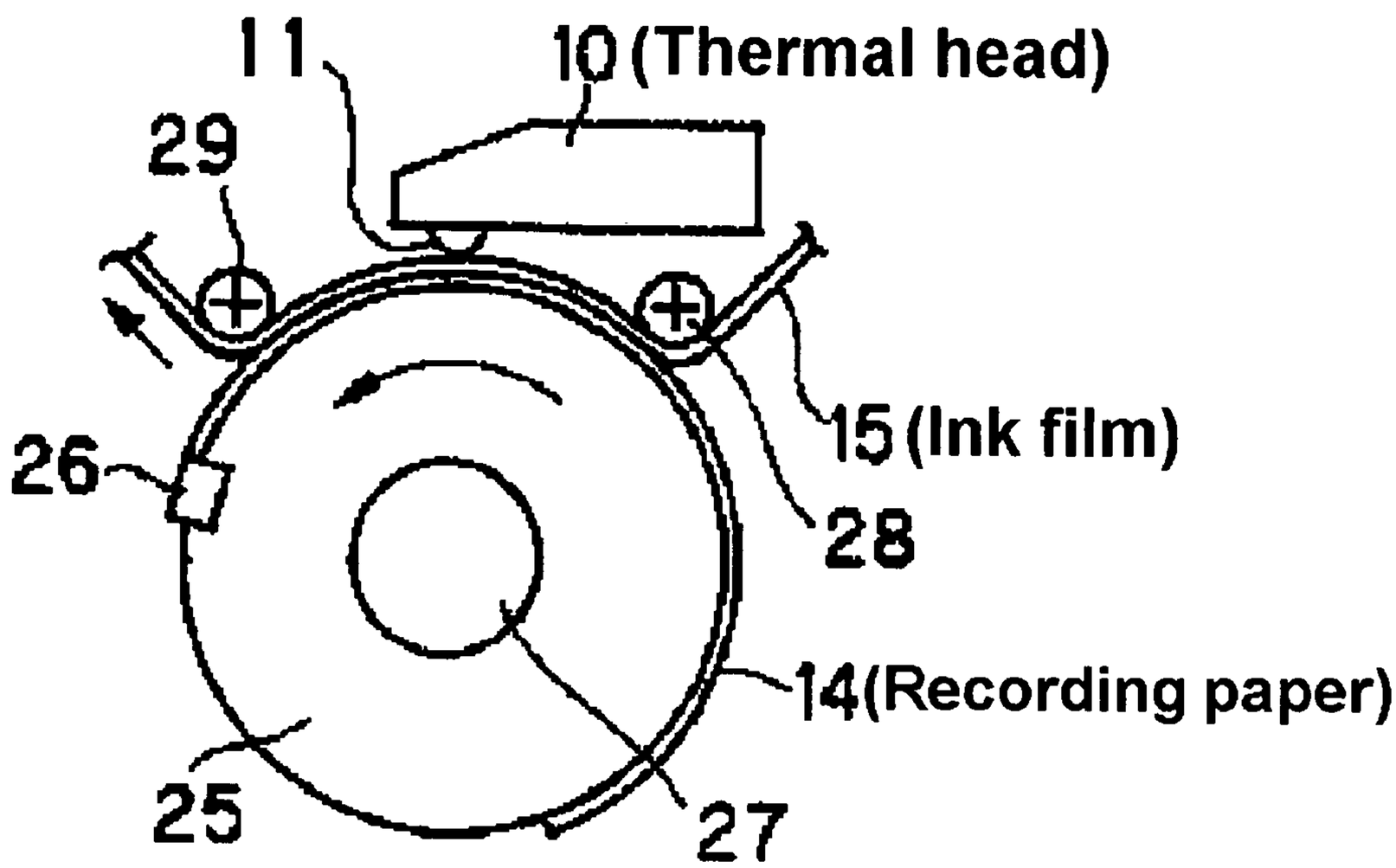

11
10 (Thermal head)
29
15 (Ink film)
26
28
14 (Recording paper)
25
27

IMAGE-FORMING METHOD USING HEAT-SENSITIVE TRANSFER SYSTEM

FIELD OF THE INVENTION

The present invention relates to an image-forming method using a thermal transfer system, which provides an image having a high density and a high image quality. Particularly, the present invention relates to an image-forming method using a thermal transfer system which enables to prevent occurrence of hollow spot-shaped dropouts in high-speed printing.

BACKGROUND OF THE INVENTION

Various heat transfer recording methods have been known so far. Among these methods, dye diffusion transfer recording systems attract attention as a process that can produce a color hard copy having an image quality closest to that of silver salt photography (see, for example, "Joho Kiroku (Hard Copy) to Sono Zairyo no Shintenkai (Information Recording (Hard Copy) and New Development of Recording Materials)" published by Toray Research Center Inc., 1993, pp. 241-285; and "Printer Zairyo no Kaihatsu (Development of Printer Materials)" published by CMC Publishing Co., Ltd., 1995, p. 180). Moreover, this system has advantages over silver salt photography: it is a dry system, it enables direct visualization from digital data, it makes reproduction simple, and the like.

In this dye diffusion transfer recording system, a heat-sensitive transfer sheet (hereinafter also referred to as an ink sheet) containing dyes is superposed on a heat-sensitive transfer image-receiving sheet (hereinafter also referred to as an image-receiving sheet), and then the ink sheet is heated by a thermal head whose exothermic action is controlled by electric signals, in order to transfer the dyes contained in the ink sheet to the image-receiving sheet, thereby recording an image information. Three colors: cyan, magenta, and yellow, are used for recording a color image by overlapping one color to other, thereby enabling transferring and recording a color image having continuous gradation for color densities.

On the other hand, hollow spot-shaped dropouts occurring at the time of high-energy printing are serious defects from the viewpoint of image quality. As a method for inhibiting occurrence of such dropouts, it is known to use a water-soluble resin as a binder containing bubbles or foaming microcapsules (JP-A-6-270559 ("JP-A" means unexamined published Japanese patent application)). However, the use of such a resin is not always sufficient for inhibition of these dropouts, and further improvements in image quality have been desired.

SUMMARY OF THE INVENTION

The present invention resides in an image-forming method, comprising the steps of:

superposing a heat-sensitive transfer sheet on a heat-sensitive transfer image-receiving sheet so that the following at least one receptor layer of the heat-sensitive transfer image-receiving sheet can be contacted with the following thermal transfer layer of the heat-sensitive transfer sheet; and

providing thermal energy given by a thermal head in accordance with image signals, thereby to form an image;

wherein the heat-sensitive transfer image-receiving sheet is transported at a speed of 125 mm/s or more during the image formation, and

wherein the heat-sensitive transfer image-receiving sheet comprises, on a support, at least one receptor layer containing a polymer latex, and at least one heat insulation layer containing hollow polymer particles but free of any resins having poor resistance to an organic solvent except for the hollow polymer particles, and

wherein the heat-sensitive transfer sheet comprises, on a support, a thermal transfer layer.

Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is an illustration of a thermal recording apparatus that can be used for heat-sensitive transfer recording according to the present invention.

10 Thermal head
11 Exothermic element array
14 Recording paper (heat-sensitive transfer image-receiving sheet)
15 Ink film (heat-sensitive transfer sheet)
25 Platen drum
26 Clamp member
27 Pulse motor
28, **29** Guide rollers

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, there is provided the following means:

(1) An image-forming method, comprising the steps of:

superposing a heat-sensitive transfer sheet on a heat-sensitive transfer image-receiving sheet so that the following at least one receptor layer of the heat-sensitive transfer image-receiving sheet can be contacted with the following thermal transfer layer of the heat-sensitive transfer sheet; and

providing thermal energy given by a thermal head in accordance with image signals, thereby to form an image;

wherein the heat-sensitive transfer image-receiving sheet is transported at a speed of 125 mm/s or more during the image formation, and

wherein the heat-sensitive transfer image-receiving sheet comprises, on a support, at least one receptor layer containing a polymer latex, and at least one heat insulation layer containing hollow polymer particles but free of any resins having poor resistance to an organic solvent except for the hollow polymer particles, and

wherein the heat-sensitive transfer sheet comprises, on a support, a thermal transfer layer;

(2) The image-forming method according to the above item (1), wherein at least one of the receptor layer and the heat insulation layer of the heat-sensitive transfer image-receiving sheet contains a water-soluble polymer;

(3) The image-forming method according to the above item (2), wherein at least one of the receptor layer and the heat insulation layer contains a compound that enables to crosslink the water-soluble polymer, and the water-soluble polymer is partly or entirely crosslinked; and

(4) The image-forming method according to any one of the above items (1) to (3), wherein the receptor layer of the heat-sensitive transfer image-receiving sheet contains an emulsion.

The present invention is explained in detail below.

1) Heat-sensitive Transfer Image-receiving Sheet

First, the heat-sensitive transfer image-receiving sheet (image-receiving sheet) is explained.

The heat-sensitive (thermal) transfer image-receiving sheet used in the present invention is provided with at least one dye-receiving layer (receptor layer) on a support, and a heat insulation layer (porous layer) between the support and the receptor layer. Moreover, an undercoat layer such as a white-background-control layer, a charge-control layer (an electrification-control layer), an adhesive layer, and a primer layer, may be provided between the receptor layer and the heat insulation layer.

The receptor layer and the heat insulation layer are preferably formed by a simultaneous double-layer coating. When the undercoat layer is provided, the receptor layer, the undercoat layer and the heat insulation layer may be formed by the simultaneous double-layer coating.

It is preferable that a curling control layer, a writing layer, and a charge-control layer be formed on the backside of the support. Each layer on the backside of the support is applied using a usual method such as a roll coating, a bar coating, a gravure coating, and a gravure reverse coating.

(Receptor Layer)

The receptor layer performs functions of receiving dyes transferred from an ink sheet and retaining images formed. In the image-receiving sheet for use in the present invention, the receptor layer contains a polymer latex. The receptor layer may be a single layer or multi layers. The receptor layer preferably contains a water-soluble polymer as described later.

<Polymer Latex>

The polymer latex used in the present invention is explained.

In the heat-sensitive transfer image-receiving sheet used in the present invention, the polymer latex used in the receptor layer is preferably a dispersion in which hydrophobic polymers comprising a monomer unit of water-insoluble vinyl chloride are dispersed as fine particles in a water-soluble dispersion medium. The dispersed state may be one in which polymer is emulsified in a dispersion medium, one in which polymer underwent emulsion polymerization, one in which polymer underwent micelle dispersion, one in which polymer molecules partially have a hydrophilic structure and thus the molecular chains themselves are dispersed in a molecular state, or the like. Latex polymers are described in "Gosei Jushi Emulsion (Synthetic Resin Emulsion)", compiled by Taira Okuda and Hiroshi Inagaki, issued by Kobunshi Kanko Kai (1978); "Gosei Latex no Oyo (Application of Synthetic Latex)", compiled by Takaaki Sugimura, Yasuo Kataoka, Souichi Suzuki, and Keishi Kasahara, issued by Kobunshi Kanko Kai (1993); Soichi Muroi, "Gosei Latex no Kagaku (Chemistry of Synthetic Latex)", issued by Kobunshi Kanko Kai (1970); Yoshiaki Miyosawa (supervisor) "Suisei Coating-Zairyo no Kaihatsu to Oyo (Development and Application of Aqueous Coating Material)", issued by CMC Publishing Co., Ltd. (2004) and JP-A-64-538, and so forth. The dispersed particles preferably have a mean particle size (diameter) of about 1 to 50,000 nm, more preferably about 5 to 1,000 nm.

The particle size distribution of the dispersed particles is not particularly limited, and the particles may have either wide particle-size distribution or monodispersed particle-size distribution.

The latex polymer for use in the present invention may be latex of the so-called core/shell type, other than ordinary latex polymer of a uniform structure. When using a core/shell type latex polymer, it is preferred in some cases that the core and the shell have different glass transition temperatures. The glass transition temperature (Tg) of the latex polymer for use in the present invention is preferably −30° C. to 100° C., more preferably 0° C. to 80° C., further more preferably 10° C. to 70° C., and especially preferably 15° C. to 60° C.

In the present invention, as a preferable embodiment of the polymer latex used in the receptor layer, there can be preferably used polyvinyl chlorides, a copolymer comprising a monomer unit of vinyl chloride such as a vinyl chloride-vinyl acetate copolymer, and a vinyl chloride acrylate copolymer. In case of the copolymer, the vinyl chloride monomer ratio is preferably in the range of from 50% to 95%. These polymers may be straight-chain, branched, or cross-linked polymers, the so-called homopolymers obtained by polymerizing single type of monomers, or copolymers obtained by polymerizing two or more types of monomers. In the case of the copolymers, these copolymers may be either random copolymers or block copolymers. The molecular weight of each of these polymers is preferably 5,000 to 1,000,000, and further preferably 10,000 to 500,000 in terms of number average molecular weight. Polymers having excessively small molecular weight impart insufficient dynamic strength to the layer containing the latex, and polymers having excessively large molecular weight bring about poor filming ability, and therefore both cases are undesirable. Crosslinkable latex polymers are also preferably used. Among the above examples, the polymer latex for use in the present invention is preferably polyvinyl chlorides, more preferably a copolymer of vinyl chloride and an acrylic ester, further preferably one having a glass transition temperature (Tg) of 30 to 80° C.

The polymer latex that can be used in the present invention is commercially available, and polymers described below may be utilized. Examples thereof include G351 and G576 (trade names, manufactured by Nippon Zeon Co., Ltd.); VINYBLAN 240, 270, 277, 375, 386, 609, 550, 601, 602, 630, 660, 671, 683, 680, 680S, 681N, 685R, 277, 380, 381, 410, 430, 432, 860, 863, 865, 867, 900, 900GT, 938 and 950 (trade names, manufactured by Nissin Chemical Industry Co., Ltd.).

These latex polymers may be used singly, or two or more of these polymers may be blended, if necessary.

In the receptor layer for use in the present invention, a ratio of the copolymer latex comprising a monomer unit of vinyl chloride occupying the whole solid content in the layer is preferably 50% or more.

In the present invention, it is preferable to prepare the receptor layer by applying an aqueous type coating solution and then drying it. The "aqueous type" so-called here means that 60% by mass or more of the solvent (dispersion medium) of the coating solution is water. As components other than water in the coating solution, water miscible organic solvents may be used, such as methyl alcohol, ethyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide, ethyl acetate, diacetone alcohol, furfuryl alcohol, benzyl alcohol, diethylene glycol monoethyl ether, and oxyethyl phenyl ether.

The polymer latex for use in the present invention preferably has a minimum film-forming temperature (MFT) of from -30 to 90° C, more preferably from 0 to 70° C. In order to control the minimum film-forming temperature, a film-forming aid may be added. The film-forming aid is also

called a temporary plasticizer, and it is an organic compound (usually an organic solvent) that reduces the minimum film-forming temperature of the polymer latex. It is described in, for example, Souichi Muroi, "Gosei Latex no Kagaku (Chemistry of Synthetic Latex)", issued by Kobunshi Kanko Kai (1970). Preferable examples of the film-forming aid are listed below, but the compounds that can be used in the present invention are not limited to the following specific examples.

Z-1: Benzyl alcohol

Z-2: 2,2,4-Trimethylpentanediol-1,3-monoisobutyrate

Z-3: 2-Dimethylaminoethanol

Z-4: Diethylene glycol

The polymer latex used in the present invention may be used (blended) with another polymer latex. Preferable examples of the another polymer latex include polylactates, polyurethanes, polycarbonates, polyesters, polyacetals, and SBR's. Among these, polyesters and polycarbonates are preferable.

In combination with the above-described polymer latex for use in the present invention, any polymer can be used. The polymer that can be used in combination is preferably transparent or translucent, and generally colorless. The polymer may be a natural resin, polymer, or copolymer; a synthetic resin, polymer, or copolymer; or another film-forming medium; and specific examples include gelatins, polyvinyl alcohols, hydroxyethylcelluloses, cellulose acetates, cellulose acetate butyrates, polyvinylpyrrolidones, caseins, starches, polyacrylic acids, polymethylmethacrylic acids, polyvinyl chlorides, polymethacrylic acids, styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, polyvinyl acetals (e.g. polyvinyl formals, polyvinyl butyrals, etc.), polyesters, polyurethanes, phenoxy resins, polyvinylidene chlorides, polyepoxides, polycarbonates, polyvinyl acetates, polyolefins, and polyamides. In the coating liquid, a binder may be dissolved or dispersed in an aqueous solvent or in an organic solvent, or may be in the form of an emulsion.

The glass transition temperature (Tg) of the binder for use in the invention is preferably in the range of −30° C. to 70° C., more preferably −10° C. to 50° C., still more preferably 0° C. to 40° C., in view of film-forming properties (brittleness for working) and image storability. A blend of two or more types of polymers can be used as the binder. When a blend of two or more polymers is used, the average Tg obtained by summing up the Tg of each polymer weighted by its proportion, is preferably within the foregoing range. Also, when phase separation occurs or when a core-shell structure is adopted, the weighted average Tg is preferably within the foregoing range.

The glass transition temperature (Tg) is calculated according to the following equation:

$$1/Tg=\Sigma(Xi/Tgi)$$

wherein, assuming that the polymer is a copolymer composed of n monomers from i=1 to i=n, Xi is a weight fraction of the i-th monomer ($\Sigma Xi=1$) and Tgi is glass transition temperature (measured in absolute temperature) of a homopolymer formed from the i-th monomer. The symbol Σ means the sum of i=1 to i=n. The value of the glass transition temperature of a homopolymer formed from each monomer (Tgi) is adopted from J. Brandrup and E. H. Immergut, "Polymer Handbook, 3rd. Edition", Wiley-Interscience (1989).

The polymer used for the binder for use in the present invention can be easily obtained by a solution polymerization method, a suspension polymerization method, an emulsion polymerization method, a dispersion polymerization method, an anionic polymerization method, a cationic polymerization method, or the like. Above all, an emulsion polymerization method in which the polymer is obtained as a latex is the most preferable. Also, a method is preferable in which the polymer is prepared in a solution, and the solution is neutralized, or an emulsifier is added to the solution, to which water is then added, to prepare an aqueous dispersion by forced stirring. For example, an emulsion polymerization method comprises conducting polymerization under stirring at about 30° C. to about 100° C. (preferably 60° C. to 90° C.) for 3 to 24 hours by using water or a mixed solvent of water and a water-miscible organic solvent (such as methanol, ethanol, or acetone) as a dispersion medium, a monomer mixture in an amount of 5 mass % to 150 mass % based on the amount of the dispersion medium, an emulsifier and a polymerization initiator. Various conditions such as the dispersion medium, the monomer concentration, the amount of initiator, the amount of emulsifier, the amount of dispersant, the reaction temperature, and the method for adding monomers are suitably determined considering the type of the monomers to be used. Furthermore, it is preferable to use a dispersant when necessary.

Generally, the emulsion polymerization method can be conducted according to the disclosures of the following documents: "Gosei Jushi Emarujon (Synthetic Resin Emulsions)" (edited by Taira Okuda and Hiroshi Inagaki and published by Kobunshi Kankokai (1978)); "Gosei Ratekkusu no Oyo (Applications of Synthetic Latexes)" (edited by Takaaki Sugimura, Yasuo Kataoka, Soichi Suzuki, and Keiji Kasahara and published by Kobunshi Kankokai (1993)); and "Gosei Ratekkusu no Kagaku (Chemistry of Synthetic Latexes)" (edited by Soichi Muroi and published by Kobunshi Kankokai (1970)). The emulsion polymerization method for synthesizing the polymer latex for use in the present invention may be a batch polymerization method, a monomer (continuous or divided) addition method, an emulsion addition method, or a seed polymerization method. The emulsion polymerization method is preferably a batch polymerization method, a monomer (continuous or divided) addition method, or an emulsion addition method in view of the productivity of latex.

The polymerization initiator may be any polymerization initiator having radical generating ability. The polymerization initiator to be used may be selected from inorganic peroxides such as persulfates and hydrogen peroxide, peroxides described in the organic peroxide catalogue of NOF Corporation, and azo compounds as described in the azo polymerization initiator catalogue of Wako Pure Chemical Industries, Ltd. Among them, water-soluble peroxides such as persulfates and water-soluble azo compounds as described in the azo polymerization initiator catalogue of Wako Pure Chemical Industries, Ltd. are preferable; ammonium persulfate, sodium persulfate, potassium persulfate, azobis(2-methylpropionamidine)hydrochloride, azobis(2-methyl-N-(2-hydroxyethyl)propionamide), and azobiscyanovaleric acid are more preferable; and peroxides such as ammonium persulfate, sodium persulfate, and potassium persulfate are especially preferable from the viewpoints of image storability, solubility, and cost.

The amount of the polymerization initiator to be added is, based on the total amount of monomers, preferably 0.3 mass % to 2.0 mass %, more preferably 0.4 mass % to 1.75 mass %, and especially preferably 0.5 mass % to 1.5 mass %.

The polymerization emulsifier to be used may be selected from anionic surfactants, nonionic surfactants, cationic surfactants, and ampholytic surfactants. Among them, anionic surfactants are preferable from the viewpoints of dispersibility and image storability. Sulfonic acid type anionic surfactants are more preferable because polymerization stability can be ensured even with a small addition amount and they have resistance to hydrolysis. Long chain alkyldiphenyl ether disulfonic acid salts (whose typical example is PELEX SS-H manufactured by Kao Corporation, trade name) are still more preferable, and low electrolyte types such as PIONIN A-43-S (manufactured by Takemoto Oil & Fat Co., Ltd., trade name) are especially preferable.

The amount of sulfonic acid type anionic surfactant as the polymerization emulsifier is preferably 0.1 mass % to 10.0 mass %, more preferably 0.2 mass % to 7.5 mass %, and especially preferably 0.3 mass % to 5.0 mass %, based on the total amount of monomers.

It is preferable to use a chelating agent in synthesizing the polymer latex to be used in the present invention. The chelating agent is a compound capable of coordinating (chelating) a polyvalent ion such as metal ion (e.g., iron ion) or alkaline earth metal ion (e.g., calcium ion), and examples of the chelate compound which can be used include the compounds described in JP-B-6-8956 ("JP-B" means examined Japanese patent publication), U.S. Pat. No. 5,053,322, JP-A-4-73645, JP-A-4-127145, JP-A-4-247073, JP-A-4-305572, JP-A-6-11805, JP-A-5-173312, JP-A-5-66527, JP-A-5-158195, JP-A-6-118580, JP-A-6-110168, JP-A-6-161054, JP-A-6-175299, JP-A-6-214352, JP-A-7-114161, JP-A-7-114154, JP-A-120894, JP-A-7-199433, JP-A-7-306504, JP-A-9-43792, JP-A-8-314090, JP-A-10-182571, JP-A-10-182570, and JP-A-11-190892.

Preferred examples of the chelating agent include inorganic chelate compounds (e.g., sodium tripolyphosphate, sodium hexametaphosphate, sodium tetrapolyphosphate), aminopolycarboxylic acid-based chelate compounds (e.g., nitrilotriacetate, ethylenediaminetetraacetate), organic phosphonic acid-based chelate compounds (e.g., compounds described in Research Disclosure, No. 18170, JP-A-52-102726, JP-A-53-42730, JP-A-56-97347, JP-A-54-121127, JP-A-55-4024, JP-A-55-4025, JP-A-55-2988, JP-A-55-126241, JP-A-55-65955, JP-A-55-65956, JP-A-57-179843, JP-A-54-61125, and West German Patent No. 1045373), polyphenol-based chelating agents, and polyamine-based chelate compounds, with aminopolycarboxylic acid derivatives being particularly preferred.

Preferred examples of the aminopolycarboxylic acid derivative include the compounds shown in the Table attached to "EDTA (—Complexane no Kagaku—) (EDTA—Chemistry of Complexane—)", Nankodo (1977). In these compounds, a part of the carboxyl groups may be substituted by an alkali metal salt such as sodium or potassium or by an ammonium salt. More preferred examples of the aminopolycarboxylic acid derivative include iminodiacetic acid, N-methyliminodiacetic acid, N-(2-aminoethyl) iminodiacetic acid, N-(carbamoylmethyl)imino diacetic acid, nitrilotriacetic acid, ethylenediamine-N,N'-diacetic acid, ethylenediamine-N,N'-di-α-propionic acid, ethylenediamine-N,N'-di-β-propionic acid, N,N'-ethylene-bis(α-o-hydroxyphenyl)glycine, N,N'-di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid, ethylenediamine-N,N'-diacetic acid-N,N'-diacetohydroxamic acid, N-hydroxyethylethylenediamine-N,N',N'-triacetic acid, ethylenediamine-N,N,N',N'-tetraacetic acid, 1,2-propylenediamine-N,N,N',N'-tetraacetic acid, d,1-2,3-diaminobutane-N,N,N',N'-tetraacetic acid, meso-2,3-diaminobutane-N,N,N',N'-tetraacetic acid, 1-phenylethylenediamine-N,N,N',N'-tetraacetic acid, d,1-1,2-diphenylethylenediamine-N,N,N',N'-tetraacetic acid, 1,4-diaminobutane-N,N,N',N'-tetraacetic acid, trans-cyclobutane-1,2-diamine-N,N,N',N'-tetraacetic acid, trans-cyclopentane-1,2-diamine-N,N,N',N'-tetraacetic acid, trans-cyclohexane-1,2-diamine-N,N,N',N'-tetraacetic acid, cis-cyclohexane-1,2-diamine-N,N,N',N'-tetraacetic acid, cyclohexane-1,3-diamine-N,N,N',N'-tetraacetic acid, cyclohexane-1,4-diamine-N,N,N',N'-tetraacetic acid, o-phenylenediamine-N,N,N',N'-tetraacetic acid, cis-1,4-diaminobutene-N,N,N',N'-tetraacetic acid, trans-1,4-diaminobutene-N,N,N',N'-tetraacetic acid, α,α'-diamino-o-xylene-N,N,N',N'-tetraacetic acid, 2-hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid, 2,2'-oxy-bis (ethyliminodiacetic acid), 2,2'ethylenedioxy-bis (ethyliminodiacetic acid), ethylenediamine-N,N'-diacetic acid-N,N'-di-α-propionic acid, ethylenediamine-N,N'-diacetic acid-N,N'-di-β-propionic acid, ethylenediamine-N,N,N',N '-tetrapropionic acid, diethylenetriamine-N,N,N',N",N"-pentaacetic acid, triethylenetetramine-N,N,N',N",N'",N'"-hexaacetic acid, and 1,2,3-triaminopropane-N,N,N',N",N'",N'",N'"-hexaacetic acid. In these compounds, a part of the carboxyl groups may be substituted by an alkali metal salt such as sodium or potassium or by an ammonium salt.

The amount of the chelating agent to be added is preferably 0.01 mass % to 0.4 mass %, more preferably 0.02 mass % to 0.3 mass %, and especially preferably 0.03 mass % to 0.15 mass %, based on the total amount of monomers. When the addition amount of the chelating agent is too small, metal ions entering during the preparation of the polymer latex are not sufficiently trapped, and the stability of the latex against aggregation is lowered, whereby the coating properties become worse. When the amount is too large, the viscosity of the latex increases, whereby the coating properties are lowered.

In the preparation of the polymer latex to be used in the present invention, it is preferable to use a chain transfer agent. As the chain transfer agent, ones described in Polymer Handbook (3rd Edition) (Wiley-Interscience, 1989) are preferable. Sulfur compounds are more preferable because they have high chain-transfer ability and because the required amount is small. Especially, hydrophobic mercaptane-based chain transfer agents such as tert-dodecylmercaptane and n-dodecylmercaptane are preferable.

The amount of the chain transfer agent to be added is preferably 0.2 mass % to 2.0 mass %, more preferably 0.3 mass % to 1.8 mass %, and especially preferably 0.4 mass % to 1.6 mass %, based on the total amount of monomers.

Besides the foregoing compounds, in the emulsion polymerization, use can be made of additives, such as electrolytes, stabilizers, thickeners, defoaming agents, antioxidants, vulcanizers, antifreezing agents, gelling agents, and vulcanization accelerators, as described, for example, in Synthetic Rubber Handbook.

In the coating solution of the polymer latex to be used in the present invention, an aqueous solvent can be used as the solvent, and a water-miscible organic solvent may optionally be used in combination. Examples of the water-miscible organic solvent include alcohols (for example, methyl alcohol, ethyl alcohol, and propyl alcohol), cellosolves (for example, methyl cellosolve, ethyl cellosolve, and butyl cellosolve), ethyl acetate, and dimethylformamide. The amount of the organic solvent to be added is preferably 50 mass % or less of the entire solvent, more preferably 30 mass % or less of the entire solvent.

Furthermore, in the polymer latex to be used in the present invention, the polymer concentration is, based on the

amount of the latex liquid, preferably 10 mass % to 70 mass %, more preferably 20 mass % to 60 mass %, and especially preferably 30 mass % to 55 mass %.

The polymer latex in the image-receiving sheet that can be used in the present invention includes a state of a gel or dried film formed by removing a part of solvents by drying after coating.

<Water-soluble Polymer>

The receptor layer preferably contains a water-soluble polymer. Herein, the "water-soluble polymer" means a polymer which dissolves, in 100 g water at 20° C., in an amount of preferably 0.05 g or more, more preferably 0.1 g or more, further preferably 0.5 g or more, and particularly preferably 1 g or more. The water-soluble polymer which can be used in the present invention is natural polymers (polysaccharide type, microorganism type, and animal type), semi-synthetic polymers (cellulose-based, starch-based, and alginic acid-based), and synthetic polymer type (vinyl type and others); and synthetic polymers including polyvinyl alcohols, and natural or semi-synthetic polymers using celluloses derived from plant as starting materials, which will be explained later, correspond to the water-soluble polymer usable in the present invention. The latex polymers recited above are not included in the water-soluble polymers which can be used in the present invention.

Among the water-soluble polymers which can be used in the present invention, the natural polymers and the semi-synthetic polymers will be explained in detail. Specific examples include the following polymers: plant type polysaccharides such as gum arabics, κ-carrageenans, τ-carrageenans, λ-carrageenans, guar gums (e.g. Supercol, manufactured by Squalon), locust bean gums, pectins, tragacanths, corn starches (e.g. Purity-21, manufactured by National Starch & Chemical Co.), and phosphorylated starches (e.g. National 78-1898, manufactured by National Starch & Chemical Co.); microbial type polysaccharides such as xanthan gums (e.g. Keltrol T, manufactured by Kelco) and dextrins (e.g. Nadex 360, manufactured by National Starch & Chemical Co.); animal type natural polymers such as gelatins (e.g. Crodyne B419, manufactured by Croda), caseins, sodium chondroitin sulfates (e.g. Cromoist CS, manufactured by Croda); cellulose-based polymers such as ethylcelluloses (e.g. Cellofas WLD, manufactured by I.C.I.), carboxymethylcelluloses (e.g. CMC, manufactured by Daicel), hydroxyethylcelluloses (e.g. HEC, manufactured by Daicel), hydroxypropylcelluloses (e.g. Klucel, manufactured by Aqualon), methylcelluloses (e.g. Viscontran, manufactured by Henkel), nitrocelluloses (e.g. Isopropyl Wet manufactured by Hercules), and cationated celluloses (e.g. Crodacel QM, manufactured by Croda); starches such as phosphorylated starches (e.g. National 78-1898, manufactured by National Starch & Chemical Co.); alginic acid-based compounds such as sodium alginates (e.g. Keltone, manufactured by Kelco) and propylene glycol alginates; and other polymers such as cationated guar gums (e.g. Hi-care 1000, manufactured by Alcolac) and sodium hyaluronates (e.g. Hyalure, manufactured by Lifecare Biomedial) (all of the names are trade names).

Gelatin is one of preferable embodiments in the present invention. Gelatin having a molecular weight of from 10,000 to 1,000,000 may be used in the present invention. Gelatin that can be used in the present invention may contain an anion such as Cl^- and SO_4^{2-}, or alternatively a cation such as Fe^{2+}, Ca^{2+}, Mg^{2+}, Sn^{2+} and Zn^{2+}. Gelatin is preferably added as a water solution.

Among the water-soluble polymers which can be used in the present invention, the synthetic polymers will be explained in detail. Examples of the acryl type include sodium polyacrylates, polyacrylic acid copolymers, polyacrylamides, polyacrylamide copolymers, and polydiethylaminoethyl(meth)acrylate quaternary salts or their copolymers. Examples of the vinyl type include polyvinylpyrrolidones, polyvinylpyrrolidone copolymers, and polyvinyl alcohols. Examples of the others include polyethylene glycols, polypropylene glycols, polyisopropylacrylamides, polymethyl vinyl ethers, polyethyleneimines, polystyrenesulfonic acids or their copolymers, naphthalenesulfonic acid condensate salts, polyvinylsulfonic acids or their copolymers, polyacrylic acids or their copolymers, acrylic acid or its copolymers, maleic acid copolymers, maleic acid monoester copolymers, acryloylmethylpropanesulfonic acid or its copolymers, polydimethyldiallylammonium chlorides or their copolymers, polyamidines or their copolymers, polyimidazolines, dicyanamide type condensates, epichlorohydrin/dimethylamine condensates, Hofmann decomposed products of polyacrylamides, and water-soluble polyesters (Plascoat Z-221, Z-446, Z-561, Z-450, Z-565, Z-850, Z-3308, RZ-105, RZ-570, Z-730 and RZ-142 (all of these names are trade names), manufactured by Goo Chemical Co., Ltd.).

In addition, highly-water-absorptive polymers, namely, homopolymers of vinyl monomers having —COOM or —SO_3M (M represents a hydrogen atom or an alkali metal) or copolymers of these vinyl monomers among them or with other vinyl monomers (for example, sodium methacrylate, ammonium methacrylate, Sumikagel L-5H (trade name) manufactured by Sumitomo Chemical Co., Ltd.) as described in, for example, U.S. Pat. No. 4,960,681 and JP-A-62-245260, may also be used.

Preferred water-soluble synthetic polymers that can be used in the present invention are polyvinyl alcohols.

The polyvinyl alcohols are explained in detail below.

Examples of completely saponificated polyvinyl alcohol include PVA-105 [polyvinyl alcohol (PVA) content: 94.0 mass % or more; degree of saponification: 98.5±0.5 mol %; content of sodium acetate: 1.5 mass % or less; volatile constituent: 5.0 mass % or less; viscosity (4 mass %; 20° C.): 5.6±0.4 CPS]; PVA-110 [PVA content: 94.0 mass %; degree of saponification: 98.5±0.5 mol %; content of sodium acetate: 1.5 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 11.0±0.8 CPS]; PVA-117 [content: 94.0 mass %; degree of saponification: 98.5±0.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 28.0±3.0 CPS]; PVA-117H [PVA content; 93.5 mass %; degree of saponification: 99.6±0.3 mol %; content of sodium acetate: 1.85 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 29.0±3.0 CPS]; PVA-120 [PVA content: 94.0 mass %; degree of saponification: 98.5±0.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 39.5±4.5 CPS]; PVA-124 [PVA content: 94.0 mass %; degree of saponification: 98.5±0.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 60.0±6.0 CPS]; PVA-124H [PVA content: 93.5 mass %; degree of saponification: 99.6±0.3 mol %; content of sodium acetate: 1.85 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 61.0±6.0 CPS]; PVA-CS [PVA content: 94.0 mass %; degree of saponification: 97.5±0.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 27.5±3.0 CPS]; PVA-CST

[PVA content: 94.0 mass %; degree of saponification: 96.0±0.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 27.0±3.0 CPS]; and PVA-HC [PVA.content: 90.0 mass %; degree of saponification: 99.85 mol % or more; content of sodium acetate: 2.5 mass %; volatile constituent: 8.5 mass %; viscosity (4 mass %; 20° C.): 25.0±3.5 CPS] (all trade names, manufactured by Kuraray Co., Ltd.), and the like.

Examples of partially saponificated polyvinyl alcohol include PVA-203 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 3.4±0.2 CPS]; PVA-204 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 3.9±0.3 CPS]; PVA-205 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 5.0±0.4 CPS]; PVA-210 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 9.0±1.0 CPS]; PVA-217 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 22.5±2.0 CPS]; PVA-220 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 30.0±3.0 CPS]; PVA-224 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 44.0±4.0 CPS]; PVA-228 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 65.0±5.0 CPS]; PVA-235 [PVA content: 94.0 mass %; degree of saponification: 88.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 95.0±15.0 CPS]; PVA-217EE [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 23.0±3.0 CPS]; PVA-217E [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 23.0±3.0 CPS]; PVA-220E [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 31.0±4.0 CPS]; PVA-224E [PVA content: 94.0 mass %; degree of saponification: 88.0±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 45.0±5.0 CPS]; PVA-403 [PVA content: 94.0 mass %; degree of saponification: 80.0±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 3.1±0.3 CPS]; PVA-405 [PVA content: 94.0 mass %; degree of saponification: 81.5±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 4.8±0.4 CPS]; PVA-420 [PVA content: 94.0 mass %; degree of saponification: 79.5±1.5 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %]; PVA-613 [PVA content: 94.0 mass %; degree of saponification: 93.5±1.0 mol %; content of sodium acetate: 1.0 mass %; volatile constituent: 5.0 mass %; viscosity (4 mass %; 20° C.): 16.5±2.0 CPS]; L-8 [PVA content: 96.0 mass %; degree of saponification: 71.0±1.5 mol %; content of sodium acetate: 1.0 mass % (ash); volatile constituent: 3.0 mass %; viscosity (4 mass %; 20° C.): 5.4±0.4 CPS] (all trade names, manufactured by Kuraray Co., Ltd.), and the like.

The above values were measured in the manner described in JIS K-6726-1977.

With respect to modified polyvinyl alcohols, those described in Koichi Nagano, et al., "Poval", Kobunshi Kankokai, Inc. are useful. The modified polyvinyl alcohols include polyvinyl alcohols modified by cations, anions, —SH compounds, alkylthio compounds, or silanols.

Examples of such modified polyvinyl alcohols (modified PVA) include C polymers such as C-118, C-318, C-318-2A, and C-506 (all being trade names of Kuraray Co., Ltd.); HL polymers such as HL-12E and HL-1203 (all being trade names of Kuraray Co., Ltd.); HM polymers such as HM-03 and HM-N-03 (all being trade names of Kuraray Co., Ltd.); Kpolymers such as KL-118, KL-318, KL-506, KM-118T, and KM-618 (all being trade names of Kuraray Co., Ltd.); M polymers such as M-115 (a trade name of Kuraray co., Ltd.); MP polymers such as MP-102, MP-202, and MP-203 (all being trade names of Kuraray Co., Ltd.); MPK polymers such as MPK-1, MPK-2, MPK-3, MPK-4, MPK-5, and MPK-6 (all being trade names of Kuraray Co., Ltd.); R polymers such as R-1130, R-2105, and R-2130 (all being trade names of Kuraray Co., Ltd.); and V polymers such as V-2250 (a trade name of Kuraray Co., Ltd.).

The viscosity of polyvinyl alcohol can be adjusted or stabilized by adding a trace amount of a solvent or an inorganic salt to an aqueous solution of polyvinyl alcohol, and there can be employed compounds described in the aforementioned reference "Poval", Koichi Nagano et al., published by Kobunshi Kankokai, pp. 144-154. For example, a coated surface quality can be improved by an addition of boric acid. The amount of boric acid added is preferably 0.01 to 40 mass % with respect to polyvinyl alcohol.

Preferred binders are transparent or semitransparent, generally colorless, and water-soluble. Examples include natural resins, polymers and copolymers; synthetic resins, polymers, and copolymers; and other media that form films: for example, rubbers, polyvinyl alcohols, hydroxyethyl celluloses, cellulose acetates, cellulose acetate butylates, polyvinylpyrrolidones, starches, polyacrylic acids, polymethyl methacrylates, polyvinyl chlorides, polymethacrylic acids, styrene/maleic acid anhydride copolymers, styrene/acrylonitrile copolymers, styrene/butadiene copolymers, polyvinylacetals (e.g., polyvinylformals and polyvinylbutyrals), polyesters, polyurethanes, phenoxy resins, polyvinylidene chlorides, polyepoxides, polycarbonates, polyvinyl acetates, polyolefins, cellulose esters, and polyamides.

In the present invention, preferred water-soluble polymers are polyvinyl alcohols and gelatin, with gelatin being most preferred.

An amount of the water-soluble polymer added to the receptor layer is preferably from 1 to 25% by mass, more preferably from 1 to 10% by mass based on the entire receptor layer.

<Crosslinking Agent>

The receptor layer preferably contains a crosslinking agent (compound capable of crosslinking a water-soluble polymer). It is preferable that the above-mentioned water-soluble polymer contained in the receptor layer is partly or entirely crosslinked with the crosslinking agent.

The crosslinking agent is required to have a plurarity of groups capable of reacting with an amino group, a carboxyl group, a hydroxyl group or the like, but the agent to be used may be suitably selected depending on the kind of the water-soluble polymer. Thus, there is no particular limitation for the kind of the crosslinking agent. It is suitable to use each of methods described in T. H. James; "THE THEORY OF THE PHOTOGRAPHIC PROCESS FOURTH EDITION", published by Macmillan Publishing Co., Inc. (1977), pp. 77 to 87, and crosslinking agents described in, for example, U.S. Pat. No. 4,678,739, col. 41; JP-A-59-116655, JP-A-62-245261, and JP-A-61-18942. Both crosslinking agents of an inorganic compound (e.g., chrome alum, boric acid and salts thereof) and crosslinking agents of an organic compound may be preferably used. Alternatively, the crosslinking agent to be used may be a mixture solution containing a chelating agent and a zirconium compound, whose pH is in the range of 1 to 7, as described in JP-A-2003-231775.

Specific examples of the crosslinking agent include epoxy-series compounds (e.g., diglycidyl ethyl ether, ethyleneglycol diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-diglycidyl cyclohexane, N,N-diglycidyl-4-glycidyloxyaniline, sorbitol polyglycidyl ether, glycerol polyglycidyl ether, compounds described in JP-A-6-329877, JP-A-7-309954 and the like, and DIC FINE EM-60 (trade name, munufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)), aldehyde-series compounds (e.g., formaldehyde, glyoxal, glutalaldehyde), active halogen-series compounds (e.g., 2,4-dichloro-4-hydroxy-1,3,5-s-triazine, and compounds described in U.S. Pat. No. 3,325,287 and the like), active vinyl-series compounds (e.g., 1,3,5-trisacryloyl-hexahydro-s-triazine, bisvinylsulfonylmethyl ether, N,N'-ethylene-bis(vinylsulfonylacetamido)ethane, and compounds described in JP-B-53-41220, JP-B-53-57257, JP-B-59-162546, JP-B-60-80846 and the like), mucohalogen acid compounds (e.g., mucochloric acid), N-carbamoylpyridinium salt compounds (e.g., (1-morpholinocarbonyl-3-pyridinio)methanesulfonate), haloamidinium salt compounds (e.g., 1-(1-chloro-1-pyridinomethylene)pyrrolidinium, 2-naphthalenesulfonate), N-methylol-series compounds (e.g., dimethylolurea, methyloldimethylhydantoin), carbodiimido compounds (e.g., polycarbodiimido compounds derived from isoholondiisocyanate as described in JP-A-59-187029 and JP-B-5-27450, carbodiimido compounds derived from tetramethylxylylene diisocyanate as described in JP-A-7-330849, multi-branch type carbodiimido compounds described in JP-A-10-30024, carbodiimido compounds derived from dicyclohexylmethane diisocyanate as described in JP-A-2000-7642, and CARBODILITE V-02, V-02-L2, V-04, V-06, E-01 and E-02 (trade names, manufactured by Nisshinbo Industries, Inc.)), oxazoline compounds (e.g., oxazoline compounds described in JP-A-2001-215653 and EPOCROS K-1010E, K-I 020E, K-1030E, K-2010E, K-2020E, K-2030E, WS-500 and WS-700 (trade names, manufactured by NIPPON SHOKUBAI CO., LTD.)), isocyanate compounds (e.g., dispersible isocyanate compounds described in JP-A-7-304841, JP-A-8-277315, JP-A-10-45866, JP-A-9-71720, JP-A-9-328654, JP-A-9-104814, JP-A-2000-194045, JP-A-2000-194237 and JP-A-2003-64149, and Duranate WB40-100, WB40-80D, WT20-100 and WT30-100 (trade names, manufactured by Asahi Kasei Corporation), CR-60N (trade name, manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)), polymer (high molecular) hardeners (e.g., compounds described in JP-A-62-234157 and the like); boric acid and salts thereof, borax, and alum.

Preferable compounds as the crosslinking agent include epoxy-series compounds, aldehyde-series compounds, active halogen-series compounds, active vinyl-series compounds, N-carbamoylpyridinium salt compounds, N-methylol-series compounds (e.g., dimethylolurea, methyloldimethylhydantoin), carbodiimido compounds, oxazoline compounds, isocyanate compounds, polymer hardeners (e.g., compounds described in JP-A-62-234157 and the like), boric acid and salts thereof, borax, and alum. More preferable crosslinking agent include epoxy-series compounds, active halogen-series compounds, active vinyl-series compounds, N-carbamoylpyridinium salt compounds, N-methylol-series compounds (e.g., dimethylolurea, methyloldimethylhydantoin), polymer hardeners (e.g., compounds described in JP-A-62-234157 and the like) and boric acid.

The above-mentioned crosslinking agent may be used singly or in combination of two or more.

The crosslinking agent that can be used in the present invention may be added to the water-soluble polymer solution in advance, or may be added at the last step for the preparation of the coating solution. Alternatively, the crosslinking agent may be added just before the coating.

The water-soluble polymer in the receptor layer is preferably cross-linked in a ratio of from 0.1 to 20 mass %, more preferably from 1 to 10 mass %, among the entire water-soluble polymer, even though the ratio varies depending on the kind of the crosslinking agent.

The addition amount of the crosslinking agent that can be used in the present invention varies depending on the kinds of the water-soluble binder and the crosslinking agent, but it is preferable that the amount is approximately in the range of from 0.1 to 50 mass parts, more preferably from 0.5 to 20 mass parts, and further more preferably from 1 to 10 mass parts, based on 100 mass parts of the water-soluble polymer contained in the constituting layer.

<Ultraviolet Absorber>

Also, in the present invention, in order to improve light resistance, an ultraviolet absorber may be added to the receptor layer. In this case, when this ultraviolet absorber is made to have a higher molecular weight, it can be secured to the receptor layer so that it can be prevented, for instance, from being diffused into the ink sheet and from being sublimated and vaporized by heating.

As the ultraviolet absorber, compounds having various ultraviolet absorber skeletons, which are widely used in the field of information recording, may be used. Specific examples of the ultraviolet absorber may include compounds having a 2-hydroxybenzotriazole type ultraviolet absorber skeleton, 2-hydroxybenzotriazine type ultraviolet absorber skeleton, or 2-hydroxybenzophenon type ultraviolet absorber skeleton. Compounds having a benzotriazole-type or triazine-type skeleton are preferable from the viewpoint of ultraviolet absorbing ability (absorption coefficient) and stability, and compounds having a benzotriazole-type or benzophenone-type skeleton are preferable from the viewpoint of obtaining a higher-molecular weight and using in a form of a latex. Specifically, ultraviolet absorbers described in, for example, JP-A-2004-361936 may be used.

The ultraviolet absorber preferably absorbs light at wavelengths in the ultraviolet region, and the absorption edge of the absorption of the ultraviolet absorber is preferably out of the visible region. Specifically, when it is added to the receptor layer to form a heat-sensitive transfer image-receiving sheet, the heat-sensitive transfer image-receiving sheet has a reflection density of, preferably, Abs 0.5 or more at 370 nm, and more preferably Abs 0.5 or more at 380 nm.

Also, the heat-sensitive transfer image-receiving sheet has a reflection density of, preferably, Abs 0.1 or less at 400 nm. If the reflection density at a wavelength range exceeding 400 nm is high, it is not preferable because an image is made yellowish.

In the present invention, the ultraviolet absorber is preferably made to have a higher molecular weight. The ultraviolet absorber has a mass average molecular weight of preferably 10,000 or more, and more preferably 100,000 or more. As a means of obtaining a higher-molecular weight ultraviolet absorber, it is preferable to graft an ultraviolet absorber on a polymer. The polymer as the principal chain preferably has a polymer skeleton less capable of being dyed than the receptor polymer to be used together. Also, when the polymer is used to form a film, the film preferably has sufficient film strength. The graft ratio of the ultraviolet absorber to the polymer principal chain is preferably 5 to 20% by mass and more preferably 8 to 15% by mass.

Also, it is more preferable that the ultraviolet-absorber-grafted polymer is made to be used in a form of a latex. When the polymer is made to be used in a form of a latex, an aqueous dispersion-system coating solution may be used in application and coating to form the receptor layer, and this enables reduction of production cost. As a method of making the latex polymer (or making the polymer latex-wise), a method described in, for example, Japanese Patent No. 3,450,339 may be used. As the ultraviolet absorber to be used in a form of a latex, the following commercially available ultraviolet absorbers may be used which include ULS-700, ULS-1700, ULS-1383MA, ULS-1635MH, XL-7016, ULS-933LP, and ULS-935LH, manufactured by Ipposha Oil Industries Co., Ltd.; and New Coat UVA-1025W, New Coat UVA-204W, and New Coat UVA-4512M, manufactured by Shin-Nakamura Chemical Co., Ltd. (all of these names are trade names).

In the case of using an ultraviolet-absorber-grafted polymer in a form of a latex, it may be mixed with a latex of the receptor polymer capable of being dyed, and the resulting mixture is coated. By doing so, a receptor layer, in which the ultraviolet absorber is homogeneously dispersed, can be formed.

The addition amount of the ultraviolet-absorber-grafted polymer or its latex is preferably 5 to 50 parts by mass, and more preferably 10 to 30 parts by mass, to 100 parts by mass of the receptor polymer latex capable of being dyed to be used to form the receptor layer.

<Emulsified Dispersion>

In the present invention, it is preferred that the receptor layer contain an emulsified dispersion (emulsion). The term "emulsification" as used herein follows the commonly used definition. According to "Kagaku Daijiten (ENCYCLOPAEDIA CHIMICA)", Kyoritsu Shuppan Co., Ltd., for example, "emulsification" is defined as "a phenomenon in which, in one liquid, another liquid which does not dissolve in the first liquid are dispersed as fine globules, to form an emulsion". In addition, the term "emulsified dispersion" refers to "a dispersion in which fine globules of one liquid are dispersed in another liquid which does not dissolve the globules". The "emulsified dispersion" preferred in the present invention is "a dispersion of oil globules in water". The content of an emulsified dispersion in the image-receiving sheet that can be use in the present invention is preferably from 0.03 g/m^2 to 25.0 g/m^2, more preferably from 1.0 g/m^2 to 20.0 g/m^2.

In the present invention, it is preferable that a high-boiling solvent be included as an oil-soluble substance in the emulsified dispersion. Examples of the high-boiling solvent preferably used include phthalic acid esters (such as dibutyl phthalate, dioctyl phthalate, and di-2-ethyl-hexyl phthalate), phosphoric or phosphonic acid esters (such as triphenyl phosphate, tricresyl phosphate, tri-2-ethylhexyl phosphate), fatty acid esters (such as di-2-ethylhexyl succinate and tributyl citrate), benzoic acid esters (such as 2-ethylhexyl benzoate and dodecylbenzoate), amides (such as N,N-diethyldodecanamide and N,N-dimethyloleinamide), alcohol and phenol compounds (such as isostearyl alcohol and 2,4-di-tert-amylphenol), anilines (such as N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffins, hydrocarbons (such as dodecylbenzene and diisopropylnaphthalene), and carboxylic acids (such as 2-(2,4-di-tert-amylphenoxy)butyric acid). Of these high-boiling solvents, phosphoric or phosphonic acid esters (such as triphenyl phosphate, tricresyl phosphate, and tri-2-ethylhexyl phosphate) are preferred over the others. In addition to such a high-boiling solvent, an organic solvent having a boiling point of 30° C. to 160° C. (such as ethyl acetate, butyl acetate, methyl ethyl ketone, cyclohexanone, methyl cellosolve acetate, or dimethylformamide) may be used as an auxiliary solvent. The content of high-boiling solvent in the emulsified dispersion is preferably from 3.0 to 25% by mass, and more preferably from 5.0 to 20% by mass.

It is preferable that the emulsified dispersion further contain an agent for imparting fastness to images and an ultraviolet absorbent. The compounds preferably used as such agents are any of the compounds represented by formulae (B), (Ph), (E-1) to (E-3), (TS-I) to (TS-VII), (TS-VIIIA), (UA) to (UE) disclosed in JP-A-2004-361936. Further, homopolymers or copolymers insoluble in water and soluble in organic solvents (preferably the compounds disclosed in JP-A-2004-361936, paragraph Nos. 0208 to 0234) may be included therein.

<Releasing Agent>

Also, a releasing agent may be compounded in the receptor layer, in order to prevent thermal fusion with the heat-sensitive transfer sheet when an image is formed. As the releasing agent, a silicone oil, a phosphate-based plasticizer, or a fluorine-series compound may be used, and the silicone oil is particularly preferably used. As the silicone oil, modified silicone oil, such as epoxy-modified, alkyl-modified, amino-modified, carboxyl-modified, alcohol-modified, fluorine-modified, alkyl aralkyl polyether-modified, epoxy/polyether-modified, or polyether-modified silicone oil, is preferably used. Among these, a reaction product between vinyl-modified silicone oil and hydrogen-modified silicone oil is preferable. The amount of the releasing agent is preferably 0.2 to 30 parts by mass, per 100 parts by mass of the receptor polymer (polymer latex and the like) which is capable of a dye in the receptor layer.

The amount of the receptor layer to be applied is preferably 0.5 to 10 g/m^2 (solid basis, hereinafter, the amount to be applied in the present specification means a value on solid basis unless otherwise noted). The film thickness of the receptor layer is preferably 1 to 20 μm.

(Heat Insulation Layer)

A heat insulation layer serves to protect the support from heat when a thermal head or the like is used to carry out a transfer operation under heating. Also, because the heat insulation layer has high cushion characteristics, a heat-sensitive transfer image-receiving sheet having high printing sensitivity can be obtained even in the case of using paper as a substrate (support). The heat insulation layer may be a

single layer, or multi-layers. The heat insulation layer is arranged at a nearer location to the support than the receptor layer.

In the image-receiving sheet for use in the present invention, the heat insulation layer contains hollow polymer particles.

The hollow polymer particles in the present invention is polymer particles having independent pores inside of the particles. Examples of the hollow polymer particles include (1) non-foaming type hollow particles obtained in the following manner: water is contained inside of a capsule wall formed of a polystyrene, acryl resin, or styrene/acryl resin and, after a coating solution is applied and dried, the water in the particles is vaporized out of the particles, with the result that the inside of each particle forms a hollow; (2) foaming type microballoons obtained in the following manner: a low-boiling point liquid such as butane and pentane is encapsulated in a resin constituted of any one of polyvinylidene chloride, polyacrylonitrile, polyacrylic acid and polyacrylate, and their mixture or polymer, and after the resin coating material is applied, it is heated to expand the low-boiling point liquid inside of the particles whereby the inside of each particle is made to be hollow; and (3) microballoons obtained by foaming the above (2) under heating in advance, to make hollow polymer particles.

These hollow polymer particles preferably have a hollow ratio of about 20 to 70%, and may be used in combinations of two or more. Specific examples of the above (1) include Rohpake 1055 manufactured by Rohm and Haas Co.; Boncoat PP-1000 manufactured by Dainippon Ink and Chemicals, Incorporated; SX866(B) manufactured by JSR Corporation; and Nippol MH5055 manufactured by Nippon Zeon (all of these product names are trade names). Specific examples of the above (2) include F-30 and F-50 manufactured by Matsumoto Yushi-Seiyaku Co., Ltd. (all of these product names are trade names). Specific examples of the above (3) include F-30E manufactured by Matsumoto Yushi-Seiyaku Co., Ltd, and Expancel 461 DE, 551 DE and 551 DE20 manufactured by Nippon Ferrite (all of these product names are trade names). The hollow polymer particles for use in the heat insulation layer may be a latex thereof.

A water-dispersible resin or water-soluble type resin is preferably contained, as a binder, in the heat insulation layer containing the hollow polymer particles. As the binder resin that can be used in the present invention, known resins such as an acryl resin, styrene/acryl copolymer, polystyrene resin, polyvinyl alcohol resin, vinyl acetate resin, ethylene/vinyl acetate copolymer, vinyl chloride/vinyl acetate copolymer, styrene/butadiene copolymer, polyvinylidene chloride resin, cellulose derivative, casein, starch, and gelatin may be used. Also, these resins may be used either singly or as mixtures.

The solid content of the hollow polymer particles in the heat insulation layer preferably falls in a range from 5 to 2,000 parts by mass when the solid content of the binder resin is 100 parts by mass. Also, the ratio by mass of the solid content of the hollow polymer particles in the coating solution is preferably 1 to 70% by mass and more preferably 10 to 40% by mass. If the ratio of the hollow polymer particles is excessively low, sufficient heat insulation cannot be obtained, whereas if the ratio of the hollow polymer particles is excessively large, the adhesion between the hollow polymer particles is reduced, posing problems, for example, powder fall or film separation.

The particle size of the hollow polymer particles is preferably 0.1 to 20 μm, more preferably 0.1 to 2 μm and particularly preferably 0.1 to 1 μm. Also, the glass transition temperature (Tg) of the hollow polymer particles is preferably 70° C. or more and more preferably 100° C. or more.

The heat insulation layer of the heat-sensitive transfer image-receiving sheet in the present invention is free of any dispersion of resins having poor resistance to an organic solvent, except for the hollow polymer particles. Incorporation of the resin having poor resistance to an organic solvent (resin having a dye-dyeing affinity) in the heat insulation layer is not preferable in view of increase in loss of image definition after image transfer. It is assumed that the color-edge definition loss increases by the reason that owing to the presence of both the resin having a dye-dyeing affinity and the hollow polymer particles in the heat insulation layer, a transferred dye that has dyed the receptor layer migrates through the heat insulation layer adjacent thereto at the lapse of time.

Herein, the term "poor resistance to an organic solvent" means that a solubility in an organic solvent (e.g., methyl ethyl ketone, ethyl acetate, benzene, toluene, xylene) is 1 mass % or more, preferably 0.5 mass % or more. For example, the above-mentioned polymer latex is included in the category of the resin having "poor resistance to an organic solvent".

The heat insulation layer preferably contains the above-mentioned water-soluble polymer. Preferable compounds of the water-soluble polymer are the same as mentioned above.

An amount of the water-soluble polymer to be added in the heat insulation layer is preferably from 1 to 75 mass %, more preferably from 1 to 50 mass % to the entire heat insulation layer.

The heat insulation layer preferably contains a gelatin. The amount of the gelatin in the coating solution for the heat insulation layer is preferably 0.5 to 14% by mass, and particularly preferably 1 to 6% by mass. Also, the coating amount of the above hollow polymer in the heat insulation layer is preferably 1 to 100 g/m^2, and more preferably 5 to 20 g/m^2.

The heat insulation layer preferably contains a crosslinking agent (compound capable of crosslinking a water-soluble polymer). The water-soluble polymer that is contained in the heat insulation layer is preferably cross-linked with the crosslinking agent. Preferable compounds as well as a preferable amount of the crosslinking agent to be used are the same as mentioned above.

A preferred ratio of a cross-linked water-soluble polymer in the heat insulation layer varies depending on the kind of the crosslinking agent, but the water-soluble polymer in the heat insulation layer is crosslinked by preferably 0.1 to 20 mass %, more preferably 1 to 10 mass %, based on the entire water-soluble polymer.

A thickness of the heat insulation layer containing the hollow polymer particles is preferably from 5 to 50 μm, more preferably from 5 to 40 μm.

(Undercoat Layer)

An undercoat layer may be formed between the receptor layer and the heat insulation layer. As the undercoat layer, for example, a white background regulation layer, a charge regulation layer, an adhesive layer or a primer layer is formed. These layers may be formed in the same manner as those described in, for example, each specification of Japanese Patent Nos. 3,585,599 and 2,925,244.

(Support)

In the present invention, a waterproof support is preferably used as the support. The use of the waterproof support makes it possible to prevent the support from absorbing moisture, whereby a fluctuation in the performance of the

receptor layer with time can be prevented. As the waterproof support, for example, coated paper or laminate paper may be used.

—Coated Paper—

The coated paper is paper obtained by coating a sheet such as base paper with various resins, rubber latexes, or high-molecular materials, on one side or both sides of the sheet, wherein the coating amount differs depending on its use. Examples of such coated paper include art paper, cast coated paper, and Yankee paper.

It is proper to use a thermoplastic resin as the resin to be applied to the surface(s) of the base paper. As such a thermoplastic resin, the following thermoplastic resins (A) to (H) may be exemplified.

(A) Polyolefin resins such as polyethylene resin and polypropylene resin; copolymer resins composed of an olefin such as ethylene or propylene and another vinyl monomer; and acrylic resin.

(B) Thermoplastic resins having an ester linkage: for example, polyester resins obtained by condensation of a dicarboxylic acid component (such a dicarboxylic acid component may be substituted with a sulfonic acid group, a carboxyl group, or the like) and an alcohol component (such an alcohol component may be substituted with a hydroxyl group, or the like); polyacrylate resins or polymethacrylate resins such as polymethylmethacrylate, polybutylmethacrylate, polymethylacrylate, polybutylacrylate, or the like; polycarbonate resins, polyvinyl acetate resins, styrene acrylate resins, styrene-methacrylate copolymer resins, vinyltoluene acrylate resins, or the like.

Concrete examples of them are those described in JP-A-59-101395, JP-A-63-7971, JP-A-63-7972, JP-A-63-7973, and JP-A-60-294862.

Commercially available thermoplastic resins usable herein are, for example, Vylon 290, Vylon 200, Vylon 280, Vylon 300, Vylon 103, Vylon GK-140, and Vylon GK-130 (products of Toyobo Co., Ltd.); Tafton NE-382, Tafton U-5, ATR-2009, and ATR-2010 (products of Kao Corporation); Elitel UE 3500, UE 3210, XA-8153, KZA-7049, and KZA-1449 (products of Unitika Ltd.); and Polyester TP-220 and R-188 (products of The Nippon Synthetic Chemical Industry Co., Ltd.); and thermoplastic resins in the Hyros series from Seiko Chemical Industries Co., Ltd., and the like (all of these names are trade names).

(C) Polyurethane resins, etc.

(D) Polyamide resins, urea resins, etc.

(E) Polysulfone resins, etc.

(F) Polyvinyl chloride resins, polyvinylidene chloride resins, vinyl chloride/vinyl acetate copolymer resins, vinyl chloride/vinyl propionate copolymer resins, etc.

(G) Polyol resins such as polyvinyl butyral; and cellulose resins such as ethyl cellulose resin and cellulose acetate resin, and

(H) Polycaprolactone resins, styrene/maleic anhydride resins, polyacrylonitrile resins, polyether resins, epoxy resins, and phenolic resins.

The thermoplastic resins may be used either alone or in combination of two or more.

The thermoplastic resin may contain a whitener, a conductive agent, a filler, a pigment or dye including, for example, titanium oxide, ultramarine blue, and carbon black; or the like, if necessary.

—Laminated Paper—

The laminated paper is a paper which is formed by laminating various kinds of resin, rubber, polymer sheets or films on a sheet such as a base paper or the like. Specific examples of the materials useable for the lamination include polyolefins, polyvinyl chlorides, polyethylene terephthalates, polystyrenes, polymethacrylates, polycarbonates, polyimides, and triacetylcelluloses. These resins may be used alone, or in combination of two or more.

Generally, the polyolefins are prepared by using a low-density polyethylene. However, for improving the thermal resistance of the support, it is preferred to use a polypropylene, a blend of a polypropylene and a polyethylene, a high-density polyethylene, or a blend of a high-density polyethylene and a low-density polyethylene. From the viewpoint of cost and its suitableness for the laminate, it is preferred to use the blend of a high-density polyethylene and a low-density polyethylene.

The blend of a high-density polyethylene and a low-density polyethylene is preferably used in a blend ratio (a mass ratio) of 1/9 to 9/1, more preferably 2/8 to 8/2, and most preferably 3/7 to 7/3. When the thermoplastic resin layer is formed on the both surfaces of the support, the back side of the support is preferably formed using, for example, the high-density polyethylene or the blend of a high-density polyethylene and a low-density polyethylene. The molecular weight of the polyethylenes is not particularly limited. Preferably, both of the high-density polyethylene and the low-density polyethylene have a melt index of 1.0 to 40 g/10 minute and a high extrudability.

The sheet or film may be subjected to a treatment to impart white reflection thereto. As a method of such a treatment, for example, a method of incorporating a pigment such as titanium oxide into the sheet or film can be mentioned.

The thickness of the support is preferably from 25 μm to 300 μm, more preferably from 50 μm to 260 μm, and further preferably from 75 μm to 220 μm. The support can have any rigidity according to the purpose. When it is used as a support for electrophotographic image-receiving sheet of photographic image quality, the rigidity thereof is preferably near to that in a support for use in color silver halide photography.

(Curling Control Layer)

When the support is exposed as it is, there is the case where the heat-sensitive transfer image-receiving sheet is made to curl by moisture and/or temperature in the environment. It is therefore preferable to form a curling control layer on the backside of the support. The curling control layer not only prevents the image-receiving sheet from curling but also has a water-proof function. For the curling control layer, a polyethylene laminate, a polypropylene laminate or the like is used. Specifically, the curling control layer may be formed in a manner similar to those described in, for example, JP-A-61-110135 and JP-A-6-202295.

(Writing Layer and Charge Controlling Layer)

For the writing layer and the charge control layer, an inorganic oxide colloid, an ionic polymer, or the like may be used. As the antistatic agent, any antistatic agents including cationic antistatic agents such as a quaternary ammonium salt and polyamine derivative, anionic antistatic agents such as alkyl phosphate, and nonionic antistatic agents such as fatty acid ester may be used. Specifically, the writing layer and the charge control layer may be formed in a manner similar to those described in the specification of Japanese Patent No. 3585585.

In the present invention, the above-described resin having poor resistance to an organic solvent or the water-soluble

polymer used in the image-receiving sheet is preferably in the form of an aqueous (water-based) dispersion.

The method of producing the heat-sensitive transfer image-receiving sheet for use in the present invention is explained below.

The heat-sensitive transfer image-receiving sheet for use in the present invention may be prepared by coating each of layers using a usual method such as a roll coating, a bar coating, a gravure coating and a gravure reverse coating, followed by drying the layers.

Alternatively, the heat-sensitive transfer image-receiving sheet for use in the present invention may be also prepared by simultaneous double-layer coating the receptor layer and the heat insulation layer on the support.

It is known that in the case of producing an image-receiving sheet composed of plural layers having different functions from each other (for example, an air cell layer, heat insulation layer, intermediate layer and receptor layer) on a support, it may be produced by applying and overlapping each layer one by one or by applying materials prepared in advance by coating a support with each layer, as shown in, for example, JP-A-2004-106283, JP-A-2004-181888 and JP-A-2004-345267. It has been known in photographic industries, on the other hand, that productivity can be greatly improved by applying plural layers simultaneously as a multilayer. For example, there are known methods such as the so-called slide coating (slide coating method) and curtain coating (curtain coating method) as described in, for example, U.S. Pat. Nos. 2,761,791, 2,681,234, 3,508,947, 4,457,256 and 3,993,019; JP-A-63-54975, JP-A-61-278848, JP-A-55-86557, JP-A-52-31727, JP-A-55-142565, JP-A-50-43140, JP-A-63-80872, JP-A-54-54020, JP-A-5-104061, JP-A-5-127305, and JP-B-49-7050; and Edgar B. Gutoff, et al., "Coating and Drying Defects: Troubleshooting Operating Problems", John Wiley & Sons Company, 1995, pp. 101-103.

In the present invention, it has been found that the productivity is greatly improved and image defects can be remarkably reduced at the same time, by using the above simultaneous multilayer coating for the production of an image-receiving sheet having a multilayer structure.

The plural layers in the present invention are structured using resins as its major components. Coating solutions forming each layer are preferably water-dispersible latexes. The solid content by mass of the resin put in a latex state in each layer coating solution is preferably in a range from 5 to 80% and particularly preferably 20 to 60%. The average particle size of the resin contained in the above water-dispersed latex is preferably 5 μm or less and particularly preferably 1 μm or less. The above water-dispersed latex may contain a known additive, such as a surfactant, a dispersant, and a binder resin, according to the need.

In the present invention, it is preferred that a laminate composed of plural layers be formed on a support and solidified just after the forming, according to the method described in U.S. Pat. No. 2,761,791. For example, in the case of solidifying a multilayer structure by using a resin, it is preferable to raise the temperature immediately after the plural layers are formed on the support. Also, in the case where a binder (e.g., a gelatin) to be gelled at lower temperatures is contained, there is the case where it is preferable to drop the temperature immediately after the plural layers are formed on the support.

In the present invention, the coating amount of a coating solution per one layer constituting the multilayer is preferably in a range from 1 g/m^2 to 500 g/m^2. The number of layers in the multilayer structure may be arbitrarily selected from a number of 2 or more. The receptor layer is preferably disposed as a layer most apart from the support.

Also, the heat-sensitive transfer image-receiving sheet for use in the present invention may be used in various applications enabling thermal transfer recording, such as heat-sensitive transfer image-receiving sheets in a form of thin sheets (cut sheets) or rolls; cards; and transmittable type manuscript-making sheets, by optionally selecting the type of support.

2) Heat-sensitive Transfer Sheet

Next, the heat-sensitive (thermal) transfer sheet (ink sheet) for use in the present invention is explained below.

The ink sheet that is used in combination with the above-mentioned heat-sensitive transfer image-receiving sheet at the time when a thermal transfer image is formed, is provided with, on a support, a thermal transfer layer containing a diffusion transfer dye (hereinafter, also referred to as "dye layer"). The ink sheet may be arbitrarily selected from any ink sheets. The heat-sensitive transfer sheet is a preferable one, which has three primary color layers containing yellow, magenta or cyan colorants, respectively, in a state that these layers are formed one after another in the direction of the major axis of the heat-sensitive transfer sheet (so that each layer has an area corresponding to the recording surface area of a heat-sensitive transfer image-receiving sheet), and which further has a protective layer transfer section that is provided after the formation of the cyan colorant layer. The content of each dye in the thermal transfer layer (dye layer) is preferably from 10 to 90 mass %, more preferably from 20 to 80 mass %.

The dye layer is applied using a usual method such as a roll coating, a bar coating, a gravure coating, and a gravure reverse coating.

A coating amount of the thermal transfer layer in the heat-sensitive transfer sheet (ink sheet) is preferably in the range of 0.1 to 1.0 g/m^2 (in solid content equivalent), and more preferably in the range of 0.15 to 0.60 g/m^2. Hereinafter, the term "coating amount" used herein is expressed by a solid content equivalent value, unless it is indicated differently in particular.

A film thickness of the thermal transfer layer is preferably in the range of 0.1 to 2.0 μm, and more preferably in the range of 0.1 to 1.0 μm.

As a support for the heat-sensitive transfer sheet, use may be made of the same as those for use in the heat-sensitive transfer image-receiving sheet, for example, polyethylene-terephthalate.

A thickness of the support is preferably in the range of 1 to 10 μm, and more preferably in the range of 2 to 10 μm. With respect to the heat-sensitive transfer sheet, there is a detailed explanation in, for example, JP-A-11-105437. The description in paragraph Nos. 0017 to 0078 of JP-A-11-105437 may be preferably incorporated by reference into the specification of the present application.

As a means for providing heat energy in the thermal transfer, any of the conventionally known providing means may be used. For example, a heat energy of about 5 to 100 mJ/mm^2 is applied by controlling recording time in a recording device such as a thermal printer (trade name: Video Printer VY-100, manufactured by Hitachi, Ltd.), whereby the expected object can be attained sufficiently.

The image-forming method of the present invention can be achieved by the similar manner to that as described in, for example, JP-A-2005-88545. In the present invention, a printing time is preferably less than 8 seconds, and more

preferably in the range of 3 to 8 seconds, from the viewpoint of shortening a time taken until a consumer gets a print.

The present invention may be utilized for printers, copying machines and the like, which employs a heat-sensitive transfer recording system.

In the present invention, the transport speed of the heat-sensitive transfer image-receiving sheet during the image formation is 125 mm/s or more, preferably from 125 mm/s to 200 mm/s, more preferably from 125 mm/s to 190 mm/s, most preferably from 125 mm/s to 175 mm/s. Herein, "mm/s" means millimeter per second. Herein, the term "transport speed" of the heat-sensitive transfer image-receiving sheet means the speed with which the heat-sensitive transfer image-receiving sheet reciprocates underneath a thermal head.

Next, a thermal printer that can be used in the thermal sublimation recording or thermal transfer recording is described in detail.

As shown in FIG. **1**, for example, a thermal printer is configured so that heat-sensitive transfer recording is performed by passing electric current through an exothermic part (exothermic element array) **11** of a thermal head **10** as a heat-sensitive transfer sheet (ink film) **15** is transported in the direction of the arrow by means of transport rollers (guide rollers) **28** and **29** and the resultant heat-sensitive transfer sheet thus-used is taken up so as to be wound in a ribbon cartridge. In the thermal transfer layer of the heat-sensitive transfer sheet **15**, owing to each of a yellow, a magenta and a cyan colorant layer is formed corresponding to the area of the recording surface of a heat-sensitive transfer image-receiving sheet (recording paper) **14**, respectively, the heat-sensitive transfer image-receiving sheet **15** is made to reciprocate underneath the thermal head **11** by switching the transport rollers **28** and **29** between the forward and backward rotational directions, and thereby all colors are given to the surface of the recording paper **14**. The term "transport speed" of the thermal transfer image-receiving sheet **14** upon the image formation means the speed with which the thermal transfer image-receiving sheet reciprocates underneath the thermal head **11**.

The present invention relates to an image-forming method using a thermal transfer system, which provides an image having a high density and a high image quality. Particularly, the present invention relates to an image-forming method using a thermal transfer system which enables to prevent occurrence of hollow spot-shaped dropouts in high-speed printing.

The present invention can provide a printing image having a high density and a high image quality available to consumers with rapidity. Particularly, the present invention can provide an image forming method, which achieves both high-speed printing in high density and reduction in image defects, such as hollow spot-shaped dropouts, at the same time.

The present invention will be described in more detail based on the following examples, but the invention is not intended to be limited thereto.

EXAMPLES

In the following Examples, the terms "part" and "%" are values by mass, unless they are indicated differently in particular.

[Production of an Ink Sheet D1]

A polyester film 6.0 μm in thickness (trade name: Lumirror, manufactured by Toray Industries, Inc.) was used as the substrate film. A heat-resistant slip layer (thickness: 1 μm) was formed on the backside of the film, and the following yellow, magenta, and cyan compositions were respectively applied as a monochromatic layer (coating amount: 1 μm^2 when the layer was dried) on the front side. Then, the following coating solution for formation of a release layer was applied on those color layers (coating amount: 0.5 g/m^2 when the layer was dried), and dried (110° C., 60 seconds). Further, the following coating solution for formation of a protective layer (coating amount: 2 g/m^2 when the layer was dried) was applied on the releasing layer, and dried (110° C., 60 seconds). Thus, a protective layer allowing thermal transfer was formed.

Yellow Composition

Dye (1)-1	2.2 parts by mass
Dye (3)-1	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Magenta Composition

Dye (4)-1	2.2 parts by mass
Dye (5)-1	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Cyan Composition

Dye (6)-1	2.2 parts by mass
Dye (6)-4	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Coating solution for formation of protective layer	
Polyester 1 described below	10 parts by mass
Polyvinyl acetal resin (S-LEC KS-1, trade name, manufactured by Sekisui Chemical Co., Ltd.)	6 parts by mass
UV absorbent acrylic copolymer (UVA635L, trade name, manufactured by BASF Japan Ltd.)	4 parts by mass
Benzotriazole UV absorbent (TINUVIN234, trade name, manufactured by Ciba-Geigy)	10 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	80 parts by mass
Coating solution for formation of releasing layer	

-continued

Coating solution for formation of protective layer	
Ionomer resin (manufactured by Mitsui Chemicals Inc.)	10 parts by mass
Water/ethanol (2/3, at mass ratio)	100 parts by mass

Polyester 1

A polyester having a number average molecular weight of 5,000 was obtained by polymerizing the following acid ingredients and diol ingredients in the following proportions (by mole).

Diethylene glycol	5 parts by mass
Tricyclodecanedimethanol (TCD-M)	45 parts by mass
Terephthalic acid	25 parts by mass
Isophthalic acid	25 parts by mass

[Production of an Ink Sheet D2]

An ink sheet D2 was prepared in the same manner as the ink sheet D1, except that the compositions of the ink layers of each single color were changed to the following compositions, respectively.

Yellow Composition

Dye (1)-2	2.2 parts by mass
Dye (3)-2	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Magenta Composition

Dye (4)-2	2.2 parts by mass
Dye (5)-2	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Cyan Composition

Dye (6)-2	2.2 parts by mass
Dye (6)-5	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

[Production of an Ink Sheet D3]

An ink sheet D3 was prepared in the same manner as the ink sheet D1, except that the compositions of the ink layers of each single color were changed to the following compositions, respectively.

Yellow Composition

Dye (7)-1	2.2 parts by mass
Dye (8)-1	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Magenta Composition

Dye (9)-1	1.0 parts by mass
Dye (10)-1	1.0 parts by mass
Dye (11)-1	2.5 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Cyan Composition

Dye (12)-1	2.2 parts by mass
Dye (13)-1	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

[Production of an Ink Sheet D4]

An ink sheet D4 was prepared in the same manner as the ink sheet D1, except that the compositions of the ink layers of each single color were changed to the following compositions, respectively.

Yellow Composition

Dye (7)-2	2.2 parts by mass
Dye (8)-2	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

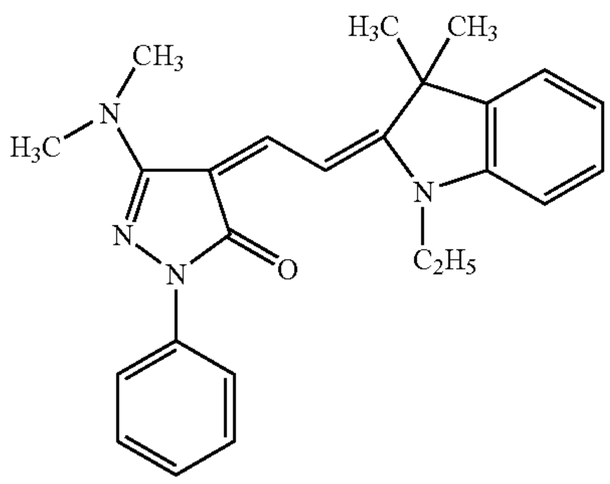
Magenta Composition

Dye (9)-2	1.0 parts by mass
Dye (10)-2	1.0 parts by mass
Dye (11)-2	2.5 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

Cyan Composition

Dye (12)-2	2.2 parts by mass
Dye (13)-2	2.3 parts by mass
Polyvinylbutyral resin (Trade name: ESLEC BX-1, manufactured by Sekisui Chemical Co., Ltd.)	4.5 parts by mass
Methyl ethyl ketone/toluene (1/1, at mass ratio)	90 parts by mass

(1)-1



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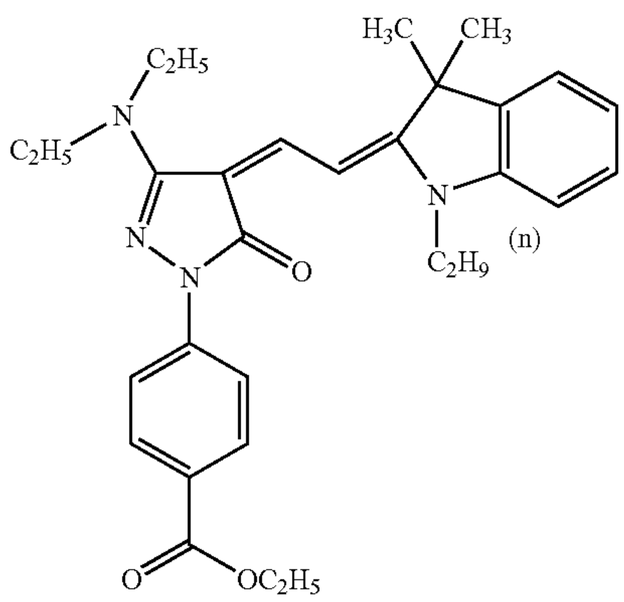

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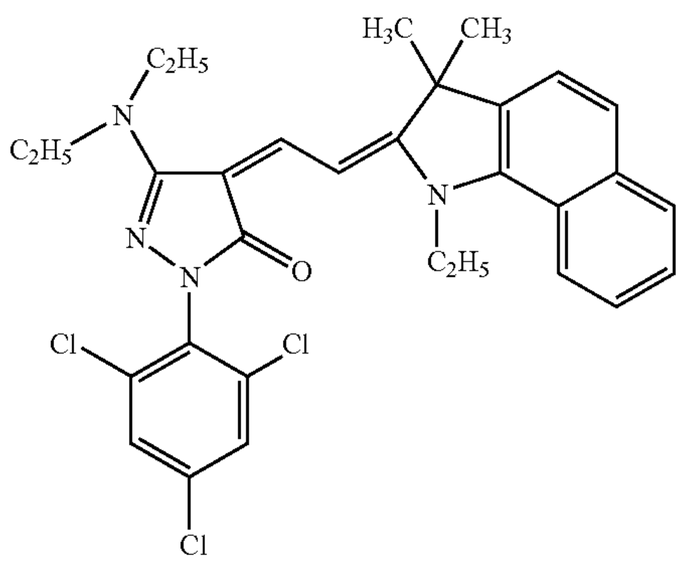

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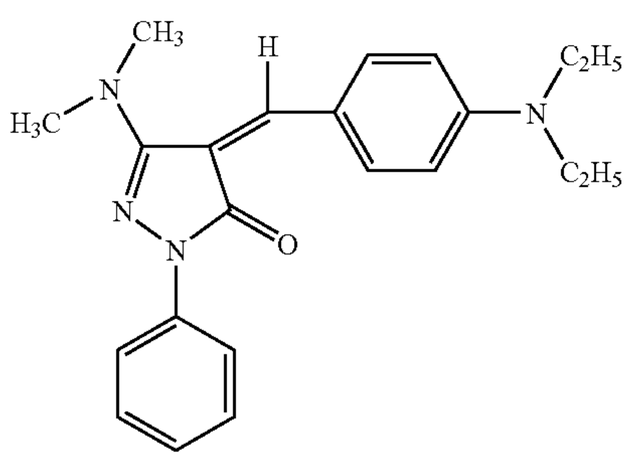

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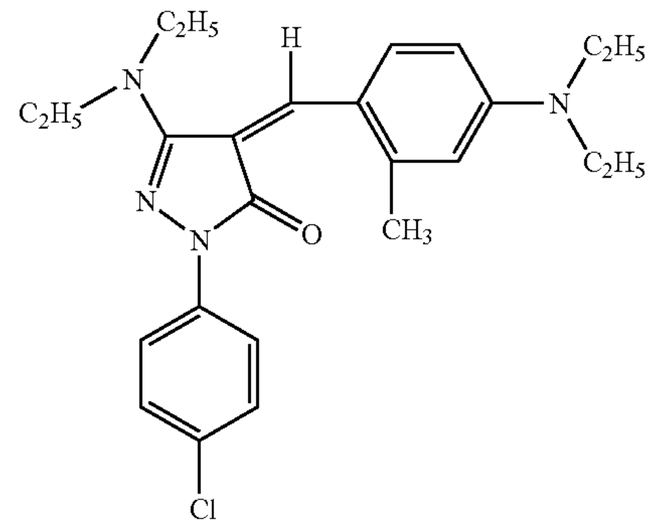

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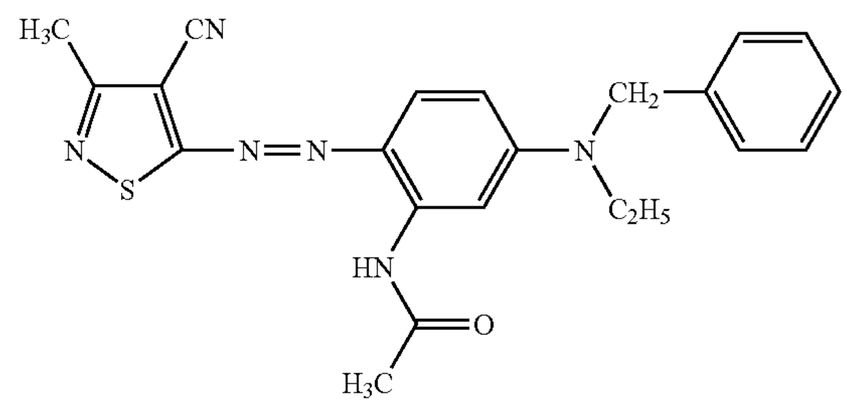

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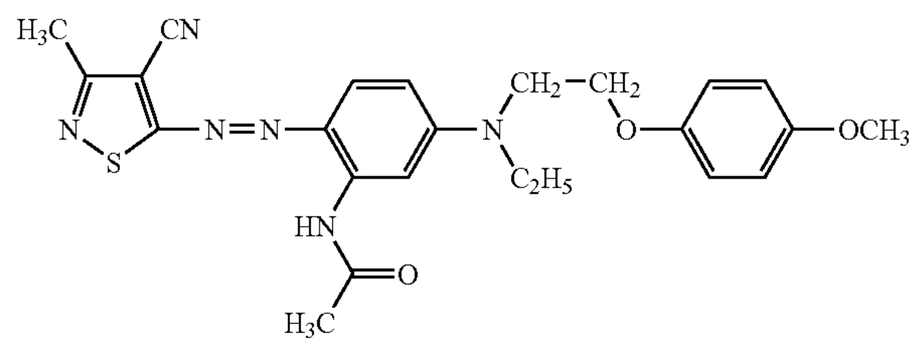

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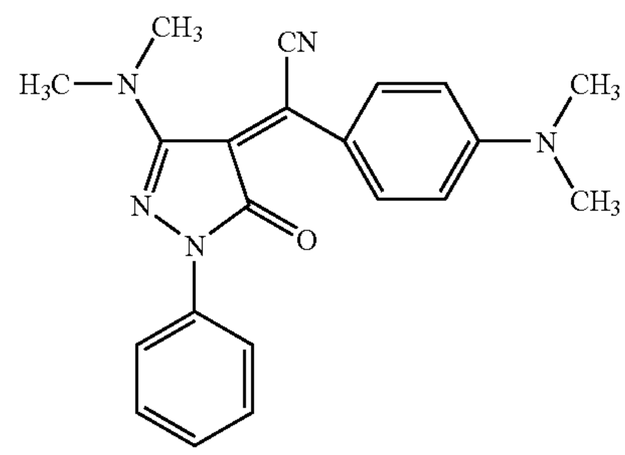

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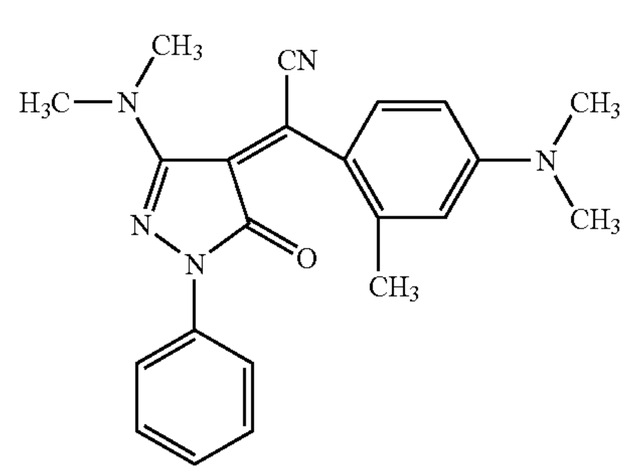

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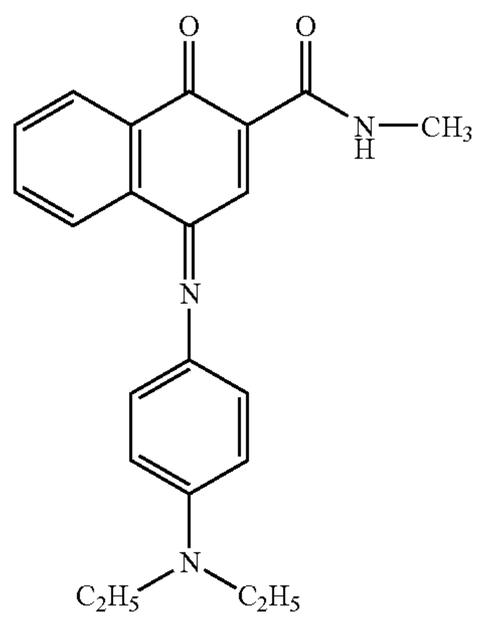

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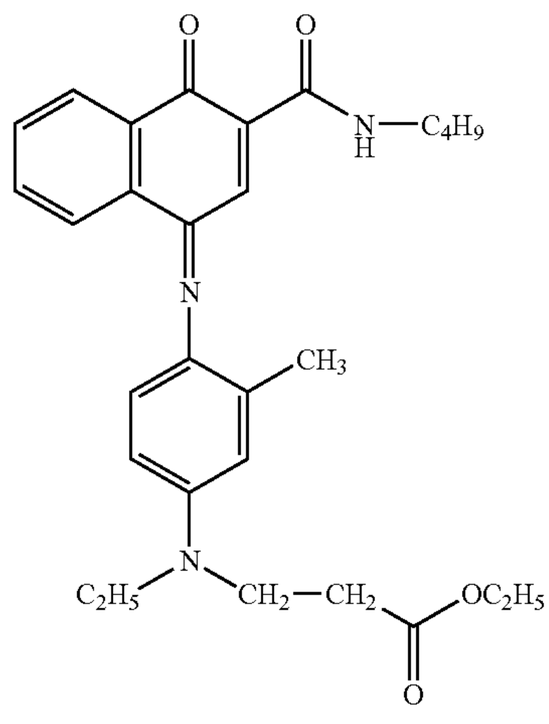

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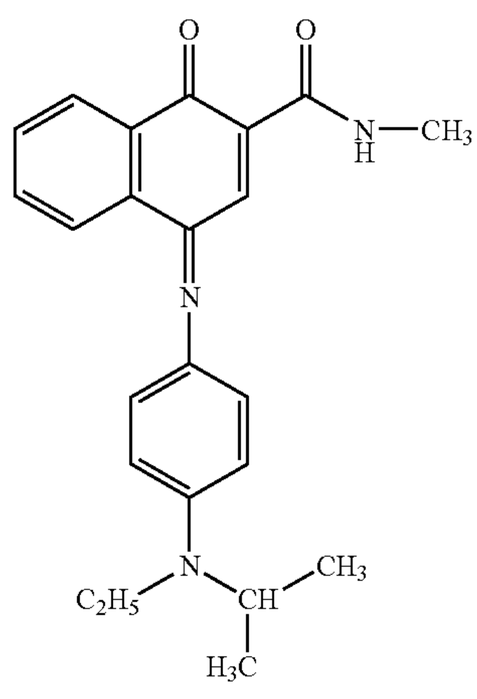

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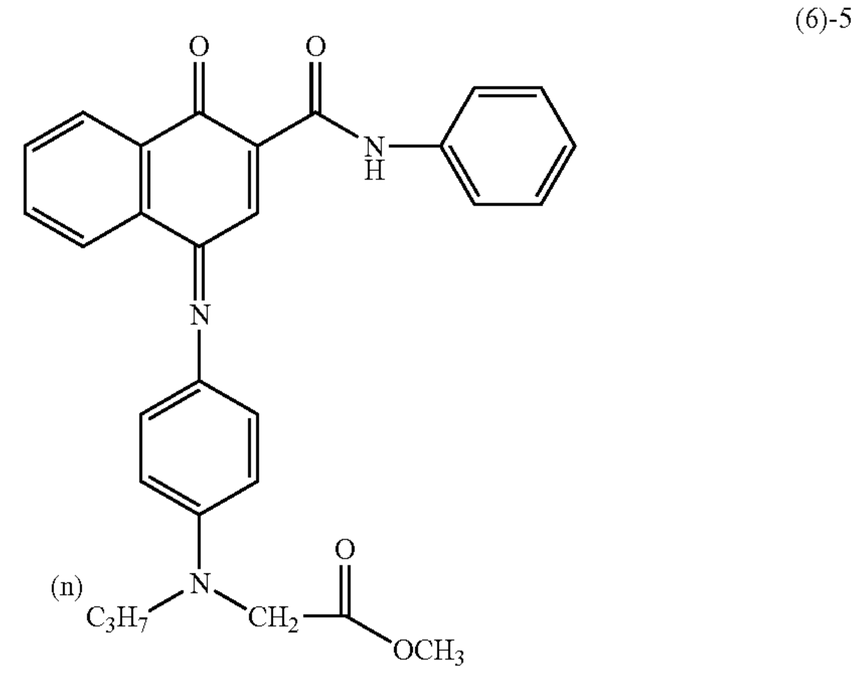

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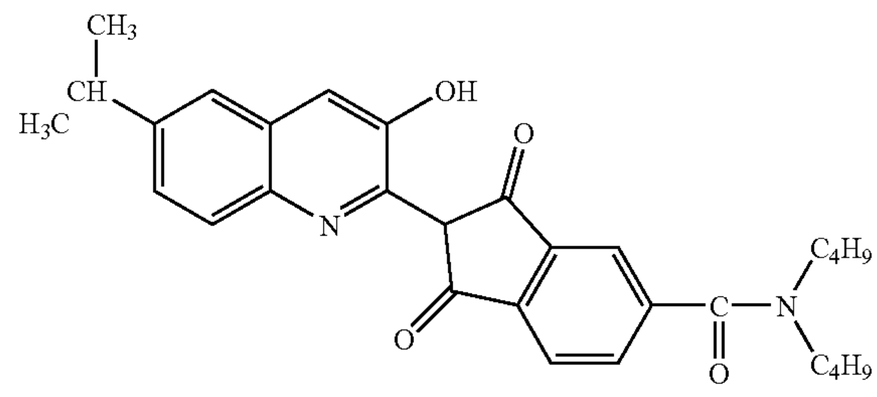

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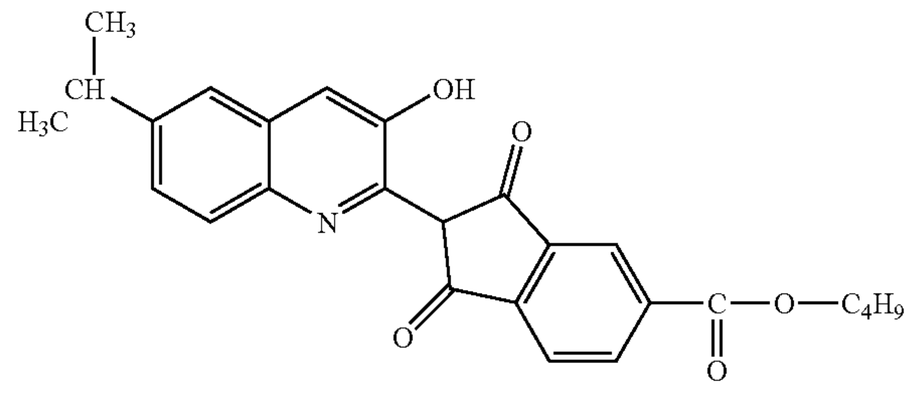

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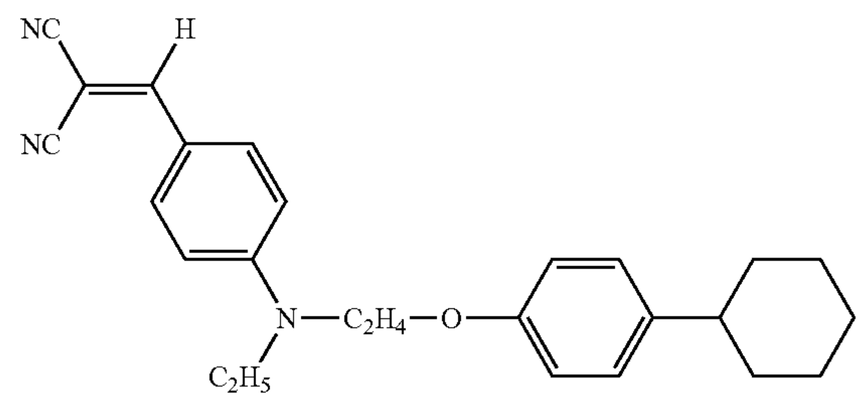

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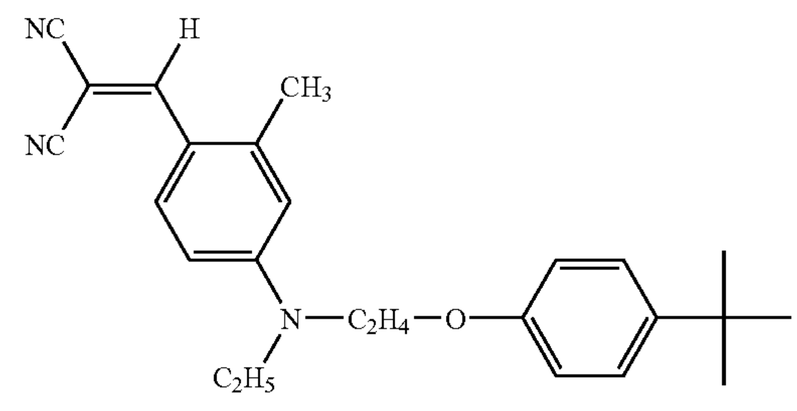

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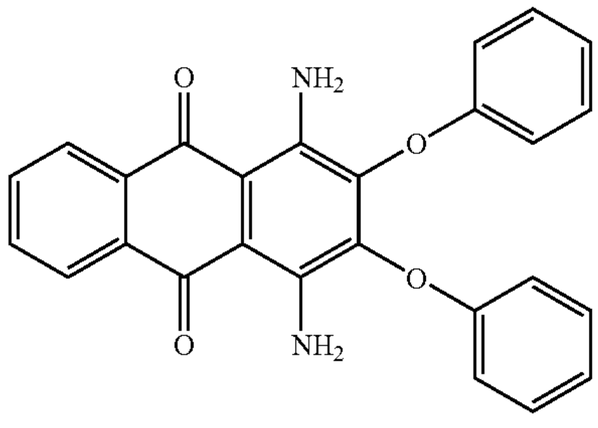

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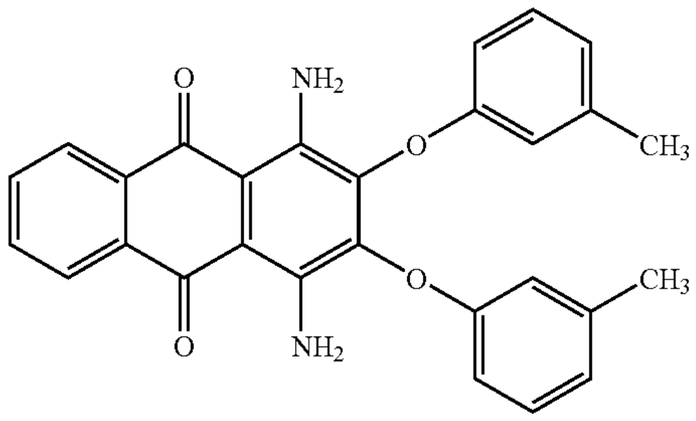

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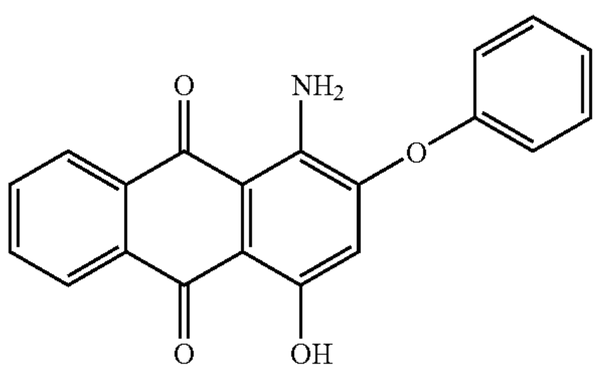

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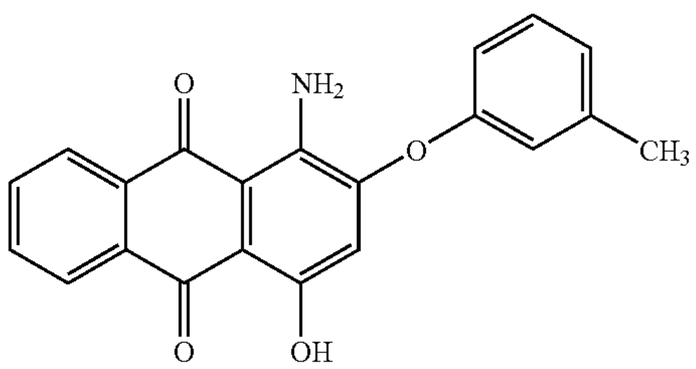

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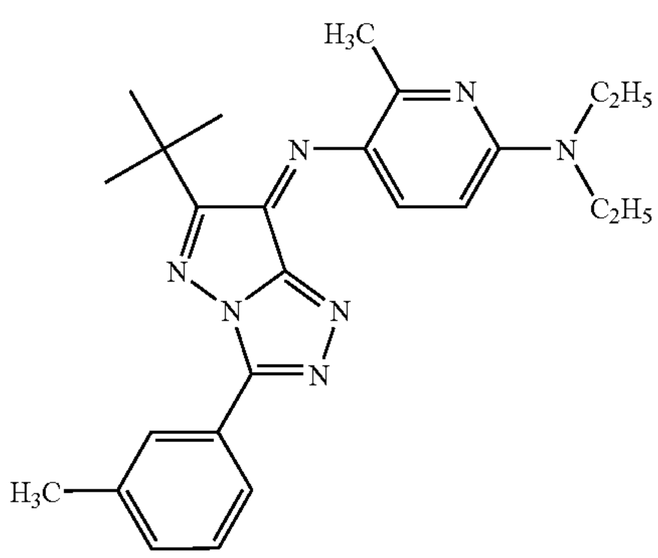

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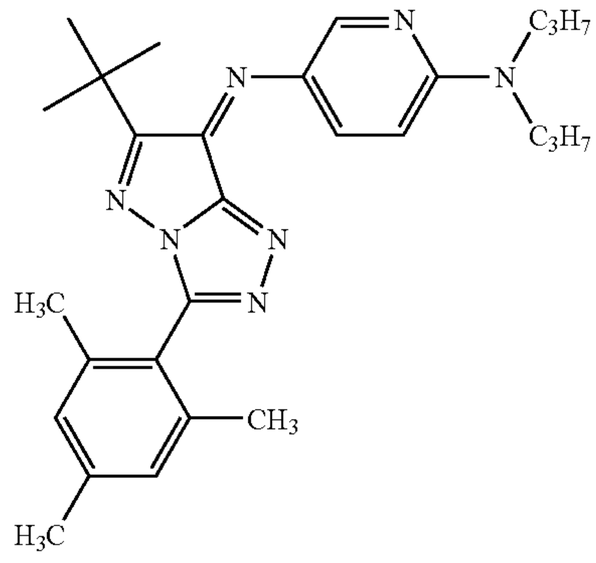

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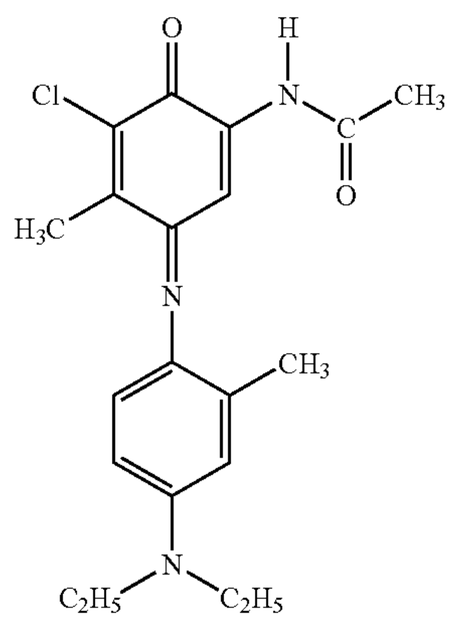

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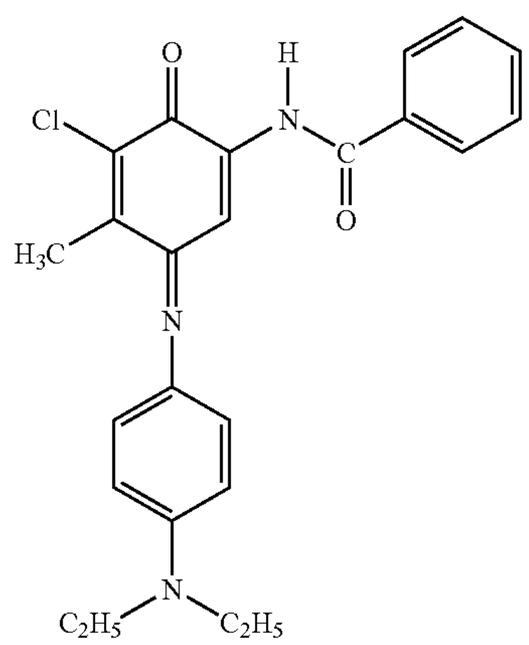

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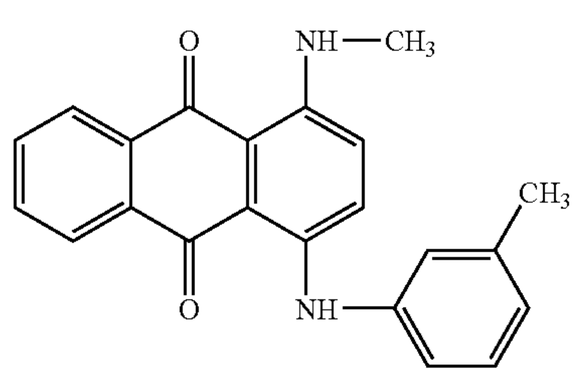

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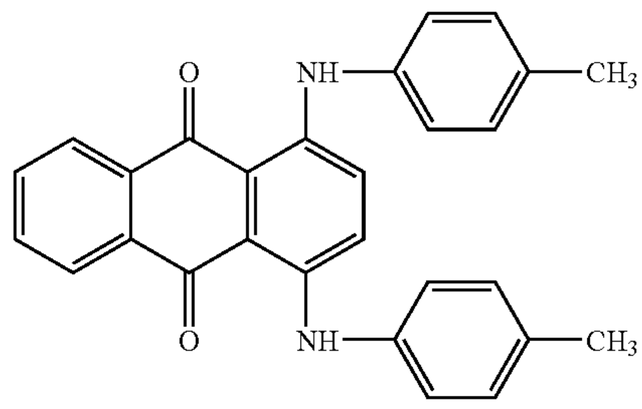


[Production of Image-receiving Sheet]

(Preparation of Support)

A pulp slurry was prepared from 50 parts by mass of hardwood kraft pulp (LBKP) of acacia origin and 50 parts by mass of hardwood kraft pulp (LBKP) of aspen origin, by beating these pulps by means of a disk refiner until Canadian standard freeness reached to 300 ml.

To the pulp slurry thus prepared were added, on a pulp basis, 1.3 mass % of modified cationic starch (CAT0304L, trade name, manufactured by Nippon NSC), 0.15 mass % of anionic polyacrylamide (DA4104, trade name, manufactured by Seiko PMC Corporation), 0.29 mass % of an alkylketene dimer (SIZEPINE K, trade name, manufactured by Arakawa Chemical Industries, Ltd.), 0.29 mass % of epoxidated behenic acid amide, and 0.32 mass % of polyamide polyamine epichlorohydrin (ARAFIX 100, trade name, manufactured by Arakawa Chemical Industries, Ltd.), and thereafter 0.12 mass % of a defoaming agent was further added.

The resulting pulp slurry was made into paper by use of a fourdrinier paper machine. In a process of drying in which the felt side of web was pressed against a drum dryer cylinder via a dryer canvas, the web thus formed was dried under a condition that the tensile strength of the dryer canvas was adjusted to 1.6 kg/cm. Then, each side of the raw paper thus made was coated with 1 g/m^2 of polyvinyl alcohol (KL-118, trade name, manufactured by Kuraray Co., Ltd.) with a size press, then, dried and further subjected to calendering treatment. Therein, the papermaking was performed so that the raw paper had a grammage (basis weight) of 157 g/m^2, and the raw paper (base paper) having a thickness of 160 μm was obtained.

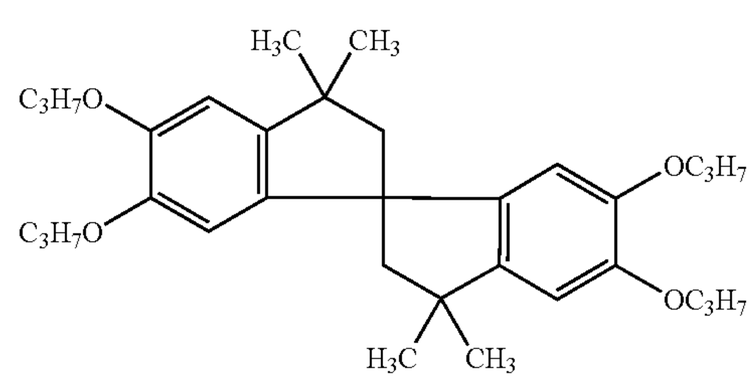
The wire side (back side) of the base paper obtained was subjected to corona discharge treatment, and thereto a resin composition, in which a high-density polyethylene having an MFR (which stands for a melt flow rate, and hereinafter has the same meaning) of 16.0 g/10 min and a density of 0.96 g/cm^3 (containing 250 ppm of hydrotalcite (DHT-4A (trade name), manufactured by Kyowa Chemical Industry Co., Ltd.) and 200 ppm of a secondary oxidation inhibitor (tris(2,4-di-t-butylphenyl)phosphite, Irugaphos 168 (trade name), manufactured by Ciba Specialty Chemicals)) and a low-density polyethylene having an MFR of 4.0 g/10 min and a density of 0.93 g/cm^3 were mixed at a ratio of 75 to 25 by mass, was applied so as to have a thickness of 21 g/m^2, by means of a melt extruder, thereby forming a thermoplastic resin layer with a mat surface. (The side to which this thermoplastic resin layer was provided is hereinafter referred to as "back side"). The thermoplastic resin layer at the back side was further subjected to corona discharge treatment, and then coated with a dispersion prepared by dispersing into water a 1:2 mixture (by mass) of aluminum oxide (ALUMINASOL 100, trade name, manufactured by Nissan Chemical Industries, Ltd.) and silicon dioxide (SNOWTEX O, trade name, manufactured by Nissan Chemical Industries, Ltd.), as an antistatic agent, so that the coating had a dry mass of 0.2 g/m^2. Subsequently, the front surface (front side) of the base paper was subjected to corona discharge treatment, and then coated with 27 g/m^2 of a low-density polyethylene having an MFR of 4.0 g/10 min and a density of 0.93 g/m^2 and containing 10 mass % of titanium oxide, by means of a melt extruder, thereby forming a thermoplastic resin layer with a specular surface.

(Preparation of Emulsified Dispersion)

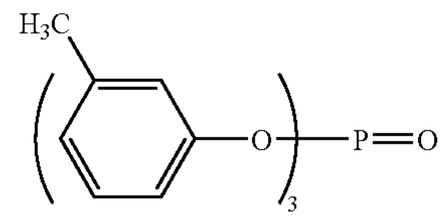
An emulsified dispersion A was prepared in the following manner. A compound A-6 was dissolved in a mixture of 42 g of a high-boiling solvent (Solv-1) and 20 ml of ethyl acetate, and the resulting solution was emulsified and dispersed in 250 g of a 20 mass % aqueous gelatin solution containing 1 g of sodium dodecylbenzenesulfonate by means of a high-speed stirring emulsification machine (dissolver). Thereto, water was added to prepare 380 g of an emulsified dispersion A.

Therein, the addition amount of compound A-6 was adjusted so that the compound would be contained in an amount of 30 mole % in the emulsified dispersion A.

A-6



Solv-1



[Production of an Image-receiving Sheet 1]

Coating solutions described below were given to the support prepared in the foregoing manner so as to form a multilayer structure having an subbing layer 1, an subbing layer 2, a heat insulation layer, and a receptor layer, by simultaneous double-layer coating, in increasing order of distance from the support, thereby making an image-receiving sheet. Compositions and application amounts of the coating solutions used herein are shown below.

Coating Solution for Subbing Layer 1

(Composition)

3% aqueous gelatin solution

NaOH for adjusting pH to 8

(Coating amount) 11 ml/m^2

Coating Solution for Subbing Layer 2

(Composition)

Styrene-butadiene latex (SR103 (trade name), manufactured by Nippon A & L Inc.)	60 parts by mass

-continued

6% aqueous solution of polyvinyl alcohol (PVA)	40 parts by mass

NaOH for adjusting pH to 8
(Coating amount) 11 ml/m^2

Coating Solution for Heat Insulation Layer (Composition)

Hollow polymer latex (MH5055 (trade name), manufactured by Zeon Corporation)	60 parts by mass
10% Gelatin aqueous solution	20 parts by mass
Emulsified dispersion A prepared in the above	20 parts by mass

NaOH for adjusting pH to 8
(Coating amount) 45 ml/m^2

Coating Solution for Receptor Layer (Composition)

Vinyl chloride-series polymer latex (VINYBLAN 900, trade name, produced by Nissin Chemical Industry Co., Ltd.)	50 parts by mass
Vinyl chloride-series polymer latex (VINYBLAN 270, trade name, produced by Nissin Chemical Industry Co., Ltd.)	20 parts by mass
10% Gelatin aqueous solution	10 parts by mass
Emulsified dispersion A prepared in the above	10 parts by mass
Microcrystalline wax (EMUSTAR-42X (trade name), manufactured by Nippon Seiro Co., Ltd.)	5 parts by mass
Hardener (VS-7)	0.2 part by mass
Water	5 parts by mass

NaOH for adjusting pH to 8
(Coating amount) 18 ml/m^2

The hardener (VS-7) used herein is the following compound. $CH_2{=}CHSO_2CH_2C({=}O){-}NHCH_2CH_2NHC({=}O){-}SO_2CH{=}CH_2$

[Production of an Image-receiving Sheet 2]

An image-receiving sheet 2 was prepares in the same manner as the image-receiving sheet 1, except that the receptor layer coating solution was changed to the following one.

Receptor Layer Coating Solution (Composition)

Vinyl chloride-vinyl acetate copolymer (#1000D, trade name, manufactured by Denki Kagaku Kogyo Kabushiki Kaisha)	100 parts by mass
Amino-modified silicone (X-22-343, trade name, manufactured by Shin-Etsu Chemical Co., Ltd.)	3 parts by mass
Epoxy-modified silicone (KF-393, trade name, manufactured by Shin-Etsu Chemical Co., Ltd.)	3 parts by mass
Toluene-methyl ethyl ketone mixture (1/1)	500 parts by mass

NaOH for adjusting pH to 8

[Image Formation]

Image outputs in size of 152 mm×102 mm was produced from a thermal transfer Printer A (DPB 1500, trade name, made by Nidec Copal Corporation) or a thermal transfer Printer B (the printer disclosed in FIG. **6** of JP-A-5-278247) by using the foregoing ink sheets and the foregoing image-receiving sheets. In the printer A, the transport speed of each heat-sensitive transfer image-receiving sheet during the image formation was 73 mm/s. In the printer B, printing was performed in a setting that the transport speed of each heat-sensitive transfer image-receiving sheet during the image formation was 125 mm/s or 150 mm/s. In this printing, the amount of heat generated by the thermal head in the printer B was adjusted so that the image output was equivalent in density gradations to that from the thermal transfer printer A. From each printer, image output was produced on 150 sheets, and the quality thereof was measured by the number of hollow spot-shaped dropouts and the average maximum density (Dmax). The term "hollow spot-shaped dropouts" as used herein means the white spots which are from 0.1 mm^2 to less than 0.5 mm^2 in size and formed by ink dropouts occurring in normally ink-transferred areas of an image-receiving sheet.

Herein, the printed output was rated in hollow spot-shaped dropout on the following 5 criteria.

5: The number of hollow spot-shaped dropouts observed in 150 sheets of image outputs is less than 5.

4: The number of hollow spot-shaped dropouts observed in 150 sheets of image outputs is from 5 to less than 10.

3: The number of hollow spot-shaped dropouts observed in 150 sheets of image outputs is from 10 to less than 20.

2: The number of hollow spot-shaped dropouts observed in 150 sheets of image outputs is from 20 to less than 30.

1: The number of hollow spot-shaped dropouts observed in 150 sheets of output pictures is 30 or more.

The Dmax was measured with a reflection densitometer.

The results obtained are shown in the following Tables 1 to 3.

Herein, the image outputs produced from the printer A are for reference.

TABLE 1

Cases of using Printer A (transport speed: 73 mm/s)

Image-receiving sheet	Ink sheet	Number of hollow spot-shaped dropouts	Dmax	Remarks
1	D1	5	2.05	Comparative Example
1	D2	5	2.07	Comparative Example
1	D3	5	2.10	Comparative Example
1	D4	5	2.09	Comparative Example
2	D1	4	2.08	Comparative Example
2	D3	5	2.05	Comparative Example

TABLE 2

Cases of using Printer B (transport speed: 125 mm/s)

Image-receiving sheet	Ink sheet	Number of hollow spot-shaped dropouts	Dmax	Remarks
1	D1	5	2.06	This invention
1	D2	5	2.06	This invention
1	D3	5	2.08	This invention

TABLE 2-continued

Cases of using Printer B (transport speed: 125 mm/s)

Image-receiving sheet	Ink sheet	Number of hollow spot-shaped dropouts	Dmax	Remarks
1	D4	5	2.07	This invention
2	D1	2	1.99	Comparative Example
2	D3	2	2.01	Comparative Example

TABLE 3

Cases of using Printer B (transport speed: 150 mm/s)

Image-receiving sheet	Ink sheet	Number of hollow spot-shaped dropouts	Dmax	Remarks
1	D1	5	2.03	This invention
1	D2	4	2.04	This invention
1	D3	5	2.06	This invention
1	D4	5	2.05	This invention
2	D1	*	1.96	Comparative Example
2	D3	1	1.94	Comparative Example

* Fusion between the ink sheet and the image-receiving sheet was observed, and there were prints failing to be output normally.

As is shown in Table 1, there was no particular problem about hollow spot-shaped dropout and Dmax when the transport was performed at an ordinary speed. However, the transport speed setting of 125 mm/s or higher proved that, while the use of the image-receiving sheet 2 as a conventional-type image-receiving sheet caused a serious increase in the number of hollow spot-shaped dropouts and didn't always contribute to sufficient Dmax. Contrary to the above, the use of image-receiving sheet as specified in the present invention ensured remarkable reduction in the number of hollow spot-shaped dropouts and enhancement of Dmax.

Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

What we claim is:

1. An image-forming method, comprising the steps of:

superposing a heat-sensitive transfer sheet on a heat-sensitive transfer image-receiving sheet so that the following at least one receptor layer of the heat-sensitive transfer image-receiving sheet can be contacted with the following thermal transfer layer of the heat-sensitive transfer sheet; and

providing thermal energy given by a thermal head in accordance with image signals, thereby to form an image;

wherein the heat-sensitive transfer image-receiving sheet is transported at a speed of 125 mm/s or more during the image formation, and

wherein the heat-sensitive transfer image-receiving sheet comprises, on a support, at least one receptor layer containing a polymer latex, and at least one heat insulation layer containing hollow polymer particles but free of any resins having poor resistance to an organic solvent except for the hollow polymer particles, and

wherein the heat-sensitive transfer sheet comprises, on a support, a thermal transfer layer.

2. The image-forming method according to claim **1**, wherein at least one of the receptor layer and the heat insulation layer of the heat-sensitive transfer image-receiving sheet contains a water-soluble polymer.

3. The image-forming method according to claim **2**, wherein at least one of the receptor layer and the heat insulation layer contains a compound that enables to crosslink the water-soluble polymer, and the water-soluble polymer is partly or entirely crosslinked.

4. The image-forming method according to claim **1**, wherein the receptor layer of the heat-sensitive transfer image-receiving sheet contains an emulsion.

* * * * *